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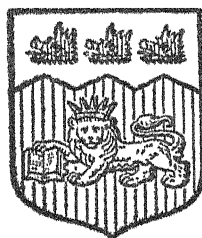
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“MOVING AXES FORMULÆ IN THE n -DIMENSIONAL SPACE.”

By

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[The present article is suggested by an attempt to generalize the result in the following example :—“ A quadric surface whose equation relative to fixed axes is at any instant

$$ax^2 + by^2 + cz^2 + 2fyz + 2gzx + 2hxy = 1$$

is of invariable form, but is rotating about the origin with the angular velocity (p, q, r) . Prove that

$$\frac{da}{d} = 2(gq - hr) \text{ etc ; etc ;}$$

$$\frac{df}{dt} = (b - c)p + gr - hq \text{ etc ; etc ;}$$

Deduce the Conditions that the surface should be of revolution.”

[Lamb's *Higher Mechanics*, Page 88.]

1° Let the (orthogonal) Cartesian Co-ordinates of a point P in the n -dimensional space be $(x_1, x_2, x_3, \dots, x_n)$ as referred to the *moving* frame of reference O— $x_1 x_2 x_3 \dots x_n$; and let the co-ordinates of a neighbouring point Q be

$$(x_1 + dx_1, x_2 + dx_2, \dots, x_n + dx_n).$$

We may regard the following as an axiomatic truth :—

Actual velocity of P = Velocity of P *relative* to the moving frame
+ the velocity which P would have in common with the frame, if rigidly connected with it.

The latter part consists of two parts,—that due to the translational motion of the frame, and the part due to its rotational motion.

With obvious notation we thus have—

$$\begin{aligned} \frac{D}{Dt} (x_1, x_2, x_3, \dots, x_n) &= \frac{d}{dt} (x_1, x_2, x_3 \dots x_n) \\ &+ (u_{01}, u_{02}, u_{03}, \dots, u_{0n}) \\ &+ \text{Rotational contribution.} \end{aligned}$$

Note here that the above equation is a brief way of writing n separate equations, one for each component.

2° To find the Rotational Contribution: Let now O be fixed and let PQ be rigidly connected to the rotating frame O- $x_1, x_2 \dots x_n$. We make use of the principle that—

The relative velocity of two points P and Q of a rigid body is at right angles to the line PQ.

Symbolically this means

$$du_1 dx_1 + du_2 dx_2 + \dots + du_n dx_n = 0.$$

Let us adopt henceforth the usual 'summation convention' that whenever a linear suffix appears twice in a term that term is to be summed up for values of the suffix 1, 2, ... n. The above then becomes

$$\begin{aligned} du_r dx_r &= 0 \\ \text{i. e. } \frac{\partial u_r}{\partial x_s} dx_s dx_r &= 0 \end{aligned}$$

Since, however, the result is true for all values of dx_r, dx_s , we must have the several coefficients zero. That is :

$$\frac{\partial u_r}{\partial x_r} = 0, \quad r=1, 2, 3, \dots n \quad \left. \vphantom{\frac{\partial u_r}{\partial x_r}} \right\} \text{I}$$

$$\text{and } \frac{\partial u_r}{\partial x_s} + \frac{\partial u_s}{\partial x_r} = 0, \quad \left. \begin{array}{l} (r, s=1, 2, 3, \dots n \\ r \neq s, \\ {}^nC_2 \text{ equations}) \end{array} \right\} \text{II}$$

From I we conclude that u_r is independent of x_r .

Next, consider any one equation of the II type,

$$\frac{\partial u_r}{\partial x_s} + \frac{\partial u_s}{\partial x_r} = 0.$$

Differentiate this with respect to one of the variables *present*, say x_s , and we have

$$\frac{\partial}{\partial x_s} \left(\frac{\partial u_r}{\partial x_s} + \frac{\partial u_s}{\partial x_r} \right) = \frac{\partial^2 u_r}{\partial x_s^2} + \frac{\partial^2 u_s}{\partial x_r \partial x_s} = 0.$$

$$\text{But } \frac{\partial u_s}{\partial x_s} = 0 \quad \text{in virtue of I,}$$

\therefore We simply have

$$\frac{\partial^2 u_r}{\partial x_s^2} = 0, \quad \left. \begin{array}{l} \text{every pair } r, s \\ r \neq s \end{array} \right\} \text{III}$$

Next, differentiate the same result

$$\frac{\partial u_r}{\partial x_s} + \frac{\partial u_s}{\partial x_r} = 0$$

with respect to any one of the *absent* variables, say x_t . And we get

$$\frac{\partial^2 u_r}{\partial x_s \partial x_t} + \frac{\partial^2 u_s}{\partial x_r \partial x_t} = 0, \quad r \neq s \neq t \quad \left. \vphantom{\frac{\partial^2 u_r}{\partial x_s \partial x_t}} \right\} \text{IV}$$

For any pair (r, s) IV represents $(n-2)$ equations; there are nC_2 such pairs. Hence the number of separate equations in IV is

$$(n-2) {}^nC_2.$$

Further, the number of different variables of the type $\frac{\partial^2 u_r}{\partial x_s \partial x_t}$

are in all

$$n. {}^{n-1}C_2 = (n-2). {}^nC_2$$

i.e. we have as many linear equations as we have the number of different variables. Each equation is simply a statement that the sum of any two of the variables is zero. The conclusion, therefore, is forced upon us that *each is zero*.

$$\text{i.e. } \frac{\partial^2 u_r}{\partial x_s \partial x_t} = 0 \quad r \neq s \neq t$$

Thus we conclude that there cannot be in the expression for μ_r , terms of higher than the first degree in x_s, x_t etc.

We may write therefore—

$$u_r = \omega_{sr} x_s \quad r \neq s.$$

where ω_{sr} are constants depending upon the *rotation* of the frame.

In virtue of IV above we must have

$$\omega_{sr} + \omega_{rs} = 0.$$

3°. Taking into account the translational motion of O, the formula for the velocity component of a point *rigidly* connected with the frame becomes

$$u_r = u_{0r} + \omega_{sr} x_s, \quad r \neq s.$$

If the point itself has a motion *relative* to the frame then the most general formula is given by

$$u_r = \frac{Dx_r}{Dt} = \frac{dx_r}{dt} + u_{0r} + \omega_{sr} x_s. \quad r \neq s.$$

$$\therefore \omega_{sr} + \omega_{rs} = 0$$

we have $\omega_{11} = \omega_{22} = \omega_{33} = \dots = 0$

Hence we may not have the restriction $r \neq s$ in

$$u_r = u_{0r} + \omega_{sr} x_s.$$

The number of constants ω_{sr} ($r \neq s$) is nC_2 , and exactly equals the number of the co-ordinate planes of the frame $O-x_1 x_2 x_3 \dots x_n$. We define that—

ω_{sr} are the components of angular velocity, perpendicular to the co-ordinate places $O-x_s x_r$.

4°. As a particular case if the frame has only rotational movement then

$$u_r = \dot{x}_r + \omega_{sr} x_s.$$

and if the point is actually fixed, then its velocity *relative* to the frame is given by $0 = \dot{x}_r + \omega_{sr} x_s$

$$\text{or} \quad \dot{x}_r = \omega_{rs} x_s.$$

5°. Application. To find the conditions that a quadric surface in the n -dimensional space should be one of revolution.

Let the equation to the quadric be

$$a_{\alpha\beta} x_\alpha x_\beta = 1. \quad \left\{ \alpha, \beta = 1, 2, \dots n. \right.$$

Let ω_{sr} be the components of the angular velocity with which it is set rotating about its frame $O-x_1 x_2 \dots x_n$ which is fixed. Impose the opposite angular velocity ω_{rs} , so that the quadric is brought to rest, but the axes are now set rotating with ω_{rs} . Then the velocity of any point $(x_1, x_2, \dots x_n)$ on the quadric *relative* to the axes is given by the formula obtained in 4° above *viz*:

$$\dot{x}_\mu = \omega_{\mu s} x_s.$$

Differentiating the equation to the quadric

$$a_{\alpha\beta} x_\alpha x_\beta = 1$$

we get

$$a_{\alpha\beta} x_\alpha x_\beta + a_{\alpha\beta} (\dot{x}_\alpha x_\beta + x_\alpha \dot{x}_\beta) = 0$$

and substituting for $\dot{x}_\alpha, \dot{x}_\beta$, we get

$$\dot{a}_{\alpha\beta} x_\alpha x_\beta + a_{\alpha\beta} (\omega_{s\alpha} x_s x_\beta + \omega_{s\beta} x_s x_\alpha) = 0$$

Now in the term $a_{\alpha\beta} \omega_{s\alpha} x_s x_\beta$ each suffix occurs twice and is therefore a 'dummy' suffix as we have to take summation over all the values from 1, 2... n . Hence a dummy suffix may be replaced by any other dummy suffix. Thus writing γ for α and α for s the term becomes

$$a_{\gamma\beta} \omega_{\alpha\gamma} x_\alpha x_\beta.$$

Similarly, the term $a_{\alpha\beta} \omega_{s\beta} x_s x_\alpha$ may be written as

$$a_{\gamma\alpha} \omega_{\beta\gamma} x_\beta x_\alpha.$$

Thus we get

$$(\dot{a}_{\alpha\beta} + a_{\gamma\beta} \omega_{\alpha\gamma} + a_{\gamma\alpha} \omega_{\beta\gamma}) x_\beta x_\alpha = 0$$

And since this result is true for all the points of the quadric, (which are infinite), it follows that the coefficient of each term = 0

$$\text{i. e.} \quad \dot{a}_{\alpha\beta} + a_{\gamma\beta} \omega_{\alpha\gamma} + a_{\gamma\alpha} \omega_{\beta\gamma} = 0$$

Remembering that

$$a_{\alpha\beta} = a_{\beta\alpha}$$

$$\text{and } \omega_{rs} = -\omega_{sr}$$

We may write the above as

$$\left. \begin{aligned} \dot{a}_{\alpha\beta} &= a_{\alpha\gamma} \omega_{\gamma\beta} + a_{\gamma\beta} \omega_{\gamma\alpha} \end{aligned} \right\} V$$

(These are ${}^nC_2 + n \equiv \frac{n(n+1)}{2}$ equations.)

Now if the quadric $a_{\alpha\beta} x_\alpha x_\beta = 1$

be a surface of revolution we must be able to choose the angular velocity (ω_{sr}) in such a manner that the rotation is about the axis of rotation,—in which case the quadric would maintain an *invariable* orientation with respect to the frame $O-x_1 x_2 \dots x_n$.

i. e. for a suitable choice of (ω_{sr})

$$\dot{a}_{\alpha\beta} = 0$$

$$\text{i. e. } a_{\gamma\alpha} \omega_{\gamma\beta} + a_{\gamma\beta} \omega_{\gamma\alpha} = 0 \quad \left. \right\} VI$$

(${}^nC_2 + n$) equations.

All the equations, however, are not independent. For, if we consider just those n equations in which α & β are equal, we have

$$\dot{a}_{11} = a_{\gamma_1} \omega_{\gamma_1} + a_{\gamma_1} \omega_{\gamma_1} = 2a_{\gamma_1} \omega_{\gamma_1} = 0$$

$$\dot{a}_{22} = 2 a_{\gamma_2} \omega_{\gamma_2} = 0$$

$$\dot{a}_{33} = 2 a_{\gamma_3} \omega_{\gamma_3} = 0$$

$$\dots \dots \dots \dots \dots$$

$$\dot{a}_{nn} = 2a_{\gamma_n} \omega_{\gamma_n} = 0$$

Adding these up and remembering that $\omega_{rs} + \omega_{sr} = 0$, we have

$$\dot{a}_{11} + \dot{a}_{22} + \dot{a}_{33} + \dots + \dot{a}_{nn} = 0, \text{ identically.}$$

∴ The number of independent equations in VI is only

$$\text{i. e. } {}^nC_2 + n - 1.$$

now there are nC_2 components of the angular velocity of the type (ω_{sr}) . Eliminating these from the ${}^nC_2 + n - 1$ equations in VI, we shall get, *in general*, $(n-1)$ independent conditions in order that the quadric

$$a_{\alpha\beta} x_\alpha x_\beta = 1$$

be a surface of revolution.

6°. Particular case : Lamb's example in three dimensions.

We have

$$d_{\alpha\beta} = a_{\gamma\alpha} \omega_{\gamma\beta} + a_{\gamma\beta} \omega_{\gamma\alpha} \left\{ \begin{array}{l} \alpha_{\mu\nu} = \alpha_{\nu\mu} \\ \omega_{\mu\nu} + \omega_{\nu\mu} = 0 \end{array} \right. \\ (\alpha, \beta = 1, 2, 3).$$

Writing the equations separately we get

$$\begin{aligned} \dot{a}_{11} &= 2 (a_{12} \omega_{21} + a_{13} \omega_{31}), \text{ etc; etc; } \\ \text{and } \dot{a}_{23} &= (a_{21} \omega_{13} + a_{22} \omega_{23}) + (a_{31} \omega_{12} + a_{33} \omega_{32}), \text{ etc; } \end{aligned}$$

Now writing as usual

$$a_{\alpha\beta} x_{\alpha} x_{\beta} \equiv ax^2 + by^2 + cz^2 + 2fyz + 2gzx + 2hxy = 1$$

We have

$$\begin{aligned} a_{11} &= a, \quad a_{22} = b, \quad a_{33} = c \\ a_{23} &= a_{32} = f, \quad a_{31} = a_{13} = g, \quad a_{12} = a_{21} = h. \end{aligned}$$

Further, in conformity with the usual notation for the angular velocity we write

$$\begin{aligned} \omega_{23} &= -\omega_{32} = \omega_1 \\ \omega_{31} &= -\omega_{13} = \omega_2 \\ \omega_{12} &= -\omega_{21} = \omega_3 \end{aligned}$$

And we obtain exactly the results given by Lamb *viz* :

$$\begin{aligned} \dot{a} &= 2 (g\omega_2 - h\omega_3) \text{ etc; etc; } \\ \dot{f} &= (b-c) \omega_1 + (g\omega_3 - h\omega_2) \text{ etc; etc. } \end{aligned}$$

Proceeding to obtain the conditions for the quadric to be of revolution, we have simply to write

$$\dot{a} = \dot{b} = \dot{c} = \dot{f} = \dot{g} = \dot{h} = 0.$$

It is easily verified that

$$\dot{a} + \dot{b} + \dot{c} = 0 \text{ identically.}$$

i. e. $(a + b + c)$ is an invariant for the change of axes.

Eliminating $\omega_1, \omega_2, \omega_3$, from the *five* independent equations we get *two* independent conditions thus :—

$$\begin{aligned} &\left. \begin{array}{l} g\omega_2 - h\omega_3 = 0 \\ h\omega_3 - f\omega_1 = 0 \\ f\omega_1 - g\omega_2 = 0 \end{array} \right\} \\ \therefore &\frac{w_1}{f^{-1}} = \frac{w_2}{g^{-1}} = \frac{w_3}{h^{-1}} \end{aligned}$$

which shows that the axis of revolution has its direction cosines proportional to $\left(\frac{1}{f}, \frac{1}{g}, \frac{1}{h}\right)$.

Next from $\dot{f} = 0$ we have

$$(b - c) \omega_1 + \begin{vmatrix} g & h \\ \omega_2 & \omega_3 \end{vmatrix} = 0$$

$$i.e. \frac{b - c}{f} + \begin{vmatrix} \frac{g}{f} & \frac{h}{f} \\ \frac{1}{g} & \frac{1}{h} \end{vmatrix} = 0$$

$$i.e. b - \frac{hf}{g} = c - \frac{fg}{h}$$

$$= a - \frac{gh}{c}, \text{ by symmetry}$$

7°. Application to two dimensions.

$$a_{\alpha\beta} x_{\alpha} x_{\beta} \equiv ax^2 + 2hxy + by^2 = 1,$$

$$a_{11} = a, a_{12} = a_{21} = h, a_{22} = b$$

$$\omega_{12} = \omega_{21} = \omega_3 = \omega \text{ say}$$

The equations

$$\dot{a}_{\alpha\beta} = a_{\gamma\alpha} \omega_{\gamma\beta} + a_{\gamma\beta} \omega_{\gamma\alpha}$$

lead to

$$\dot{a} = \dot{a}_{11} = a_{21} \omega_{21} + a_{21} \omega_{21} = -2h\omega$$

$$\dot{b} = \dot{a}_{22} = a_{12} \omega_{12} + a_{12} \omega_{12} = 2h\omega$$

and

$$\dot{h} = \dot{a}_{12} = a_{11} \omega_{12} + a_{22} \omega_{21} = (a - b)\omega$$

Thus

$$\dot{a} = \dot{b} = \dot{h} = 0$$

yield

$$-2h\omega = 0$$

$$+2h\omega = 0$$

and

$$(a - b)\omega = 0.$$

Notice that it becomes *unnecessary* to eliminate ω , and *therefore* we get *two* conditions, and *not one* condition (as we might have been led to anticipate by the general formula *viz.* $n-1$ conditions).

Thus the quadric in two dimensions becomes one of revolution *i.e.* the ellipse becomes a circle if $a - b = 0$ and $h = 0$.

Notice incidentally that from

$$\dot{a} = -2h\omega$$

$$\dot{b} = 2h\omega$$

$$\dot{h} = (a - b)\omega$$

we also deduce that $(a + b)$ and $(ab - h^2)$ are invariant expressions for a change of rectangular axes.

8°. Summary of results:—

(1). The motion of the rigid frame of reference $0 - x_1 x_2 \dots x_n$ in the n -dimensional space (and hence of any rigid body of

n dimensions) is specified by two entities u and ω ; where u is a vector of translational motion having n components

$$u_r, \quad r = 1, 2, 3 \dots n;$$

and ω stands for the angular velocity which is of the nature of an anti-symmetrical tensor having nC_2 components

$$\omega_{sr}, \quad r, s = 1, 2, 3 \dots n$$

ω_{sr} represents the component perpendicular to the co-ordinate plane $0-x_s x_r$. It just happens that in the space of three dimensions the angular velocity has also exactly *three* components. In two dimensional motion the angular velocity has only one component.

(2). The formula for the velocity of any moving point $(x_1, x_2, \dots x_n)$ as referred to the moving frame is

$$u_r = \dot{x}_r + u_{or} + \omega_{sr} x_s, \quad r = 1, 2, \dots n.$$

(3). The conditions for the quadric

$$a_{\alpha\beta} x_\alpha x_\beta = 1$$

to be surface of revolution, are $n-1$ in number, and they are to be obtained by eliminating the nC_2 components ω_{sr} from the equations

$$\dot{a}_{\alpha\beta} = a_{\gamma\alpha} \omega_{\gamma\beta} + a_{\gamma\beta} \omega_{\gamma\alpha}.$$

These are ${}^nC_2 + n$ in number, but are only ${}^nC_2 + n-1$ independent relations in virtue of the identical result that

$$\dot{a}_{11} + \dot{a}_{22} + \dot{a}_{33} + \dots + \dot{a}_{nn} = 0.$$

(4) The number of conditions in two dimensions, however, is *two* (and not one) since it is found unnecessary to eliminate ω .

(5) Rotation in the n -dimensional space, to repeat the statement for emphasis, is specified by the angular velocity which is an anti-symmetrical tensor having nC_2 components (ω_{sr}) each perpendicular to the corresponding co-ordinate plane $0-x_s x_r$.

A CHAIN OF THEOREMS RELATING TO COLLINEAR AND CONCYCLIC POINTS.

By

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1. It is well-known that the feet of the perpendiculars drawn on the sides of a triangle from any point O on the circumcircle are collinear. Given four points on the circle, they can be taken in sets of three in four ways. We will show that the feet of the perpendiculars from any point O on the circle to the four pedal lines of O with respect to the four triangles are in a line called the pedal line of O with respect to the four points. We may state a similar theorem again for five points on the circle and so on. The general theorem for any number of points on the circle was proved and developed by the writer in the *Journal of the Indian Mathematical Society* (Vol. XIX. 1932. pp. 267-272). The method adopted was by reciprocating a particular case of another chain of theorems (Coolidge: *A Treatise on the circle and the Sphere*. 1916. p. 92. Th. 164.) concerning any number of lines in a plane, the particular case being when the lines are all tangents to a parabola. The object of this paper is to connect these two chains of theorems by inversion. Incidentally, a third chain of theorems is obtained, which seems to be new and worthy of notice.

2. These new theorems may be stated as follows. Let O be a fixed point and l a fixed straight line not passing through O . Let A_1, A_2, A_3 be any three points on l . Then, the centres of the three circles $OA_1A_2, OA_2A_3, OA_3A_1$ lie on a circle passing through O . Let us denote this circle by $(A_1A_2A_3)$. Again, let there be four points A_1, A_2, A_3, A_4 on l . The centres of the four circles $(A_2A_3A_4), (A_3A_4A_1), (A_4A_1A_2), (A_1A_2A_3)$ lie on a circle passing through O , this circle being denoted by $(A_1A_2A_3A_4)$. In general, given n points A_1, A_2, \dots, A_n on l , the centres of the n circles, each associated with a set of $n-1$ of the n points, lie on circle passing through O .

3. To prove this, we require the theorem concerning any number of tangents to a parabola, referred to above. Given any four coplanar lines, the circumcircles of the four triangles formed by them pass through the Miquel point, which is the focus of the unique parabola touching the four lines. The additional fact in which we

are interested is that the four circumcentres are concyclic with the Miquel point. The circle so defined may be called the centre-circle of the four lines. Now, if five lines are given, they can be taken in sets of four in five ways and the centres of the five centre-circles are again concyclic, giving the centre-circle of five lines, and so on. The extension to any number of lines in the plane being assumed (Coolidge : loc. cit.), we remark that, if all the lines be not of general position, but are tangents to a parabola, the centre-circles obtained at any stage all pass through the focus. Now, let us describe a parabola touching the given straight line l and having O for the focus. The parabola may be fixed by one more tangent which may be chosen to be an arbitrary line l_1 through A_1 . Let l_1 cut the circle OA_1A_2 in B and BA_2 cut the circle OA_2A_3 in C . Then BA_2 , CA_3 are tangents to the parabola and O is the Miquel point of the lines l , l_1 , BA_2 , CA_3 . Thus, the centre-circle of these four lines contains the circumcentres of the triangles OA_1A_2 , OA_2A_3 , OA_3A_1 and passes through O . Again, to these four lines add a fifth, namely, the tangent (other than l) from A_4 to the parabola. The circles $(A_2A_3A_4)$, $(A_3A_4A_1)$, etc., become the centre-circles of sets of four from the five lines and hence their centres are concyclic with O . We may, thus, continue to take more points on the line l and by considering the tangents from them to the parabola, prove the theorem of art. 2.

4. A simple independent proof can also be given by the use of polar co-ordinates, if we observe that at any stage, instead of taking the centres of the system of circles, we may take the points on these circles diametrically opposite to O . Obviously, these may be proved to be concyclic, in turn. Let O be the origin and the line from O perpendicular to l be the initial line, so that the equation of l may be written $r \cos \theta = p$. Let the points A_i be given by $(p \sec \alpha_i, \alpha_i)$. Then, the equation of the circle OA_1A_2 is

$$r = p \sec \alpha_1 \sec \alpha_2 \cos (\theta - \alpha_1 - \alpha_2)$$

which shows that the point on this circle diametrically opposite to O has co-ordinates

$$(p \sec \alpha_1 \sec \alpha_2, \alpha_1 + \alpha_2).$$

Similarly writing down the co-ordinates of the points diametrically opposite to O on the circles OA_2A_3 , OA_3A_1 , we easily verify that these points lie again on the circle passing through O and whose equation is

$$r = p \sec \alpha_1 \sec \alpha_2 \sec \alpha_3 \cos (\theta - \alpha_1 - \alpha_2 - \alpha_3)$$

The proof of the general case is now obvious and the theorem is established.

5. Now, invert with O as centre. The line l and the points A_1, A_2, A_3 , are transformed into a circle L through O and points

a_1, a_2, a_3 , on L . The circles OA_1A_2 , OA_2A_3 , OA_3A_1 go over into the sides of the triangle $a_1 a_2 a_3$. A diameter of a circle being orthogonal to it, the point on the circle $OA_1 A_2$ diametrically opposite to O is inverted into the foot of the perpendicular from O on the side $A_1 A_2$. Thus, the theorem proved above shows that the feet of the perpendiculars from O on the sides of $a_1 a_2 a_3$ are collinear. Again, the point diametrically opposite to O on the circle through the points diametrically opposite to O of OA_1A_2 , OA_2A_3 , OA_3A_1 , inverts into the foot of the perpendicular from O on the pedal line of O with respect to $a_1 a_2 a_3$. Thus, again, from the theorem of art 4, it follows by inversion, that given four points $a_1 a_2 a_3 a_4$ on a circle through O , the feet of the perpendiculars from O on the four pedal lines of O with respect to $a_2 a_3 a_4$, $a_3 a_4 a_1$, etc., are collinear. The general theorem for n points on a circle is clearly seen to be true by successive inversion.

6. We may also obtain other results by inverting the theorem of pedal lines, if we choose the centre of inversion to be an arbitrary point on the circle. The following is easily proved. Let A, B, C, D be any four collinear points and O any other point. Then, the circles through D, O orthogonal to the circles OAB, OBC, OCA cut them respectively in three points lying on a circle passing through O . Let us denote this circle by $D (ABC)$. The theorem that the pedal lines of each of four concyclic points with respect to the remaining three pass through a fixed point, gives on inversion the theorem that the circles $D (ABC), A (BCD), B (CAD), C (DAB)$ are coaxal. The result of taking any other point of the plane as the centre of inversion is not so elegant or interesting.

RESISTANCE OF A GENERAL ELLIPSOID MOVING
IN A VISCOUS FLUID.

By

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In a paper published in the *Proceedings of the Benares Mathematical Society*, Vol. II, 1920, I had tackled the problem of uniform motion of an ellipsoid of revolution through a viscous fluid and had, by considering the *complete* equations of motion, derived the conditions of fluid motion and the expression for the resistance experienced by the spheroid. My object in the present paper has merely been to deduce an expression for the resistance to uniform motion of a general ellipsoid (having small ellipticities). For this purpose I have taken the results of my previous paper as guides and employed the method of polynomials in obtaining the solutions to the complete equations of motion. I intend to obtain a more satisfactory form of the solutions in a subsequent work and here I have only to express my thankfulness to the late Dr. Ganesh Prasad who had directed my attention to these problems.

Let the equation of the ellipsoid be

$$\frac{x^2}{a^2} + \frac{y^2}{b^2} + \frac{z^2}{c^2} = 1 \quad , \quad . \quad . \quad . \quad . \quad (1)$$

where $a > b > c$, and let $\varepsilon_1, \varepsilon_2, \varepsilon_3$ denote halves of the squares of the eccentricities of its three principal sections. If

$$\rho^2 = x^2 + y^2 + z^2,$$

then this equation can be put as

$$\rho = a \left(1 - \frac{\varepsilon_1}{a^2} y^2 - \frac{\varepsilon_2}{a^2} z^2 \right) \quad (2)$$

approximately, upto terms in first degree in ε_1 and ε_2 . We shall consider the case when ε_1 and ε_2 as well as ka are small quantities, k standing for $(\text{velocity})/2 \nu$ for the solid.

To start with, let the ellipsoid move parallel to the x -axis with a uniform velocity U . Obviously the expressions for the component-velocities u, v, w , and pressure p of the fluid motion for an ellipsoid differ from those of a sphere in possessing some additional terms involving the ϵ 's. Following the method of polynomials we assume that these additional terms for u, v, w are of the form

$$\Sigma a_n \rho^{-n}, \Sigma b_n \rho^{-n}, \Sigma c_n \rho^{-n} \quad (3)$$

respectively, where the a 's, b 's and c 's are functions of x, y and z , and each summation extends over a finite number of terms only.

Now, the corresponding terms as obtained by me for the motion of an ellipsoid of revolution (having the longest axis $2a$ for its axis of revolution) when simplified of exponential factors, are (*loc. cit.*)

$$U \in \left[\left(-\frac{3}{5} \frac{a}{\rho} - \frac{9}{20} \frac{a^3}{\rho^3} - \frac{9}{20} \frac{a^5}{\rho^5} \right) + x^2 \left(-\frac{3}{5} \frac{a}{\rho^3} - \frac{9a^3}{10\rho^5} + \frac{9}{2} \frac{a^5}{\rho^7} \right) + x^4 \left(\frac{15}{4} \frac{a^3}{\rho^7} - \frac{21}{4} \frac{a^5}{\rho^9} \right) \right], \quad (4)$$

$$U \in x y \left[\left(-\frac{3}{5} \frac{a}{\rho^3} - \frac{3}{20} \frac{a^3}{\rho^5} + \frac{9}{4} \frac{a^5}{\rho^7} \right) + x^2 \left(\frac{15}{4} \frac{a^3}{\rho^7} - \frac{21}{4} \frac{a^5}{\rho^9} \right) \right]. \quad (5)$$

$$U \in x z \left[\left(-\frac{3}{5} \frac{a}{\rho^3} - \frac{3}{20} \frac{a^3}{\rho^5} + \frac{9}{4} \frac{a^5}{\rho^7} \right) + x^2 \left(\frac{15}{4} \frac{a^3}{\rho^7} - \frac{21}{4} \frac{a^5}{\rho^9} \right) \right]. \quad (6)$$

respectively. And since $x^2 = \rho^2 - y^2 - z^2$, these lead us to assume that for the general ellipsoid

$$\begin{aligned} \Sigma a_n \rho^{-n} = & A_1 \rho^{-1} + (A_3 + A_{31} y^2 + A_{32} z^2) \rho^{-3} + (A_5 + A_{51} y^2 + A_{52} z^2) \rho^{-5} \\ & + (A_{71} y^2 + A_{72} z^2 + A_{73} y^4 + A_{74} z^4 + A_{75} y^2 z^2) \rho^{-7} \\ & + (A_{91} y^4 + A_{92} z^4 + A_{93} y^2 z^2) \rho^{-9}, \quad (7) \end{aligned}$$

$$\begin{aligned} \Sigma b_n \rho^{-n} = & xy \left[B_3 \rho^{-3} + B_5 \rho^{-5} + (B_7 + B_{71} y^2 + B_{72} z^2) \rho^{-7} \right. \\ & \left. + (B_{91} y^2 + B_{92} z^2) \rho^{-9} \right], \quad (8) \end{aligned}$$

$$\begin{aligned} \Sigma c_n \rho^{-n} = & xz \left[C_3 \rho^{-3} + C_5 \rho^{-5} + (C_7 + C_{71} y^2 + C_{72} z^2) \rho^{-7} \right. \\ & \left. + (C_{91} y^2 + C_{92} z^2) \rho^{-9} \right]. \quad (9) \end{aligned}$$

These assumed values of u, v, w have to satisfy the following conditions

- (i) the equations of fluid motion;
(ii) $u = U, v = 0, w = 0$ on the ellipsoid; and
(iii) $u = 0, v = 0, w = 0$ at infinity.

It is easy to see from the form of the values assumed that the third condition is fulfilled. It remains therefore to determine such values of the constants as shall be in accord with the first two conditions. If p be eliminated from the hydrodynamical equations of motion by cross-differentiation, we get

$$\begin{aligned} \nabla^2 \left(\frac{\partial u}{\partial y} - \frac{\partial v}{\partial x} \right) = & \frac{1}{\nu} \left[\frac{\partial}{\partial y} \left\{ (u-U) \frac{\partial u}{\partial x} + v \frac{\partial u}{\partial y} + w \frac{\partial u}{\partial z} \right\} \right. \\ & \left. - \frac{\partial}{\partial x} \left\{ (u-U) \frac{\partial v}{\partial x} + v \frac{\partial v}{\partial y} + w \frac{\partial v}{\partial z} \right\} \right], \quad (11) \end{aligned}$$

$$\begin{aligned} \nabla^2 \left(\frac{\partial u}{\partial z} - \frac{\partial w}{\partial x} \right) = & \frac{1}{\nu} \left[\frac{\partial}{\partial z} \left\{ (u-U) \frac{\partial u}{\partial x} + v \frac{\partial u}{\partial y} + w \frac{\partial u}{\partial z} \right\} \right. \\ & \left. - \frac{\partial}{\partial x} \left\{ (u-U) \frac{\partial w}{\partial x} + v \frac{\partial w}{\partial y} + w \frac{\partial w}{\partial z} \right\} \right]. \quad (12) \end{aligned}$$

$$\text{and} \quad \frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} + \frac{\partial w}{\partial z} = 0 \quad . \quad . \quad . \quad . \quad . \quad (13)$$

We substitute the assumed values in (11), (12), and (13), replace x^2 wherever it occurs by $(\rho^2 - y^2 - z^2)$, simplify and equate the coefficients of similar terms from both sides. As the result thereof we obtain *twenty* independent equations involving the *twenty-nine* unknown constants introduced above. In all these calculations terms in second and higher degrees in k and the ϵ 's have been neglected. For the remaining *nine* equations we turn to the second condition of (10); that is we put $u = U$, $v = 0$, $w = 0$ and $\rho =$ the right-hand side of (2), and equate the coefficients of similar terms as before. Thus we arrive at just the sufficient number of equations which lead to the following values of the constants:

$$\begin{aligned} A_1 &= -\frac{3}{5} Ua (\epsilon_1 + \epsilon_2); \quad A_3 = \frac{6}{5} Ua^3 (\epsilon_1 + \epsilon_2); \\ A_{31} &= A_{32} = \frac{3}{20} Ua (\epsilon_1 + \epsilon_2); \quad A_5 = -\frac{3}{5} Ua^5 (\epsilon_1 + \epsilon_2); \\ A_{51} &= -\frac{3}{20} Ua^3 (37 \epsilon_1 + 7 \epsilon_2); \quad A_{52} = -\frac{3}{20} Ua^3 (7 \epsilon_1 + 37 \epsilon_2); \\ A_{71} &= \frac{3}{4} Ua^5 (7 \epsilon_1 + \epsilon_2); \quad A_{72} = \frac{3}{4} Ua^5 (\epsilon_1 + 7 \epsilon_2); \\ A_{73} &= \frac{15}{4} Ua^3 \epsilon_1; \quad A_{74} = \frac{15}{4} Ua^3 \epsilon_2; \quad A_{75} = A_{73} + A_{74}; \\ A_{91} &= -\frac{21}{4} Ua^5 \epsilon_1; \quad A_{92} = -\frac{21}{4} Ua^5 \epsilon_2; \quad A_{93} = A_{91} + A_{92} \quad . \quad . \quad (14) \\ B_3 &= C_3 = -\frac{3}{10} Ua (\epsilon_1 + \epsilon_2); \\ B_5 &= \frac{3}{20} Ua^3 (17 \epsilon_1 + 7 \epsilon_2); \quad C_5 = \frac{3}{20} Ua^3 (7 \epsilon_1 + 17 \epsilon_2); \\ B_7 &= -\frac{3}{4} Ua^5 (3 \epsilon_1 + \epsilon_2); \quad C_7 = -\frac{3}{4} Ua^5 (\epsilon_1 + 3 \epsilon_2); \\ B_{71} &= C_{71} = -\frac{15}{4} Ua^3 \epsilon_1; \quad B_{72} = C_{72} = -\frac{15}{4} Ua^3 \epsilon_2; \\ B_{91} &= C_{91} = \frac{21}{4} Ua^5 \epsilon_1; \quad B_{92} = C_{92} = \frac{21}{4} Ua^5 \epsilon_2 \quad . \quad . \quad . \quad (15) \end{aligned}$$

These conditions determine the state of fluid motion due to the uniform translation of the general ellipsoid along the x -axis. Let us represent the results by

$$u = U f_1 (x, y, z, a, \epsilon_1, \epsilon_2) + U \phi_1 (x, y, z, a), \quad . \quad . \quad . \quad (16)$$

$$v = U f_2 (x, y, z, a, \epsilon_1, \epsilon_2) + U \phi_2 (x, y, z, a), \quad . \quad . \quad . \quad (17)$$

$$w = U f_3 (x, y, z, a, \epsilon_1, \epsilon_2) + U \phi_3 (x, y, z, a), \quad . \quad . \quad . \quad (18)$$

where the ϕ 's denote the results for the sphere and the f 's the additional parts for the ellipsoid. Using these values of u, v, w , we find

that the resistance experienced by the ellipsoid is parallel to the x -axis and is given by

$$F_x = -6 \pi \mu U a \left(1 + \frac{3}{4} k a - \frac{2}{5} \varepsilon_1 - \frac{2}{5} \varepsilon_2 \right). \quad (19)$$

This result agrees, upto this degree of approximation, with that obtained by C. W. Oseen [Cf. equation (7), *Archiv der Mathematik und Physik*, Bd. 24, 1915, pp. 108-114], although Prof. Oseen had started from *incomplete* equations of motion. This was expected because his equations could give results only upto the first degree in k . Further, if the term in ka be dropped, (19) would lead to Oberbeck's result upto this approximation [*Crelle's Journal*, t. LXXXI, 1876].

Proceeding in the same manner as before we can get, when the ellipsoid is moving parallel to the y -axis with uniform velocity V ,

$$u = V f_3(y, z, x, b, \varepsilon_3, -\varepsilon_1) + V \phi_3(y, z, x, b), \quad (20)$$

$$v = V f_1(y, z, x, b, \varepsilon_3, -\varepsilon_1) + V \phi_1(y, z, x, b), \quad (21)$$

$$w = V f_2(y, z, x, b, \varepsilon_3, -\varepsilon_1) + V \phi_2(y, z, x, b), \quad (22)$$

leading to

$$F_y = -6 \pi \mu V b \left(1 + \frac{3}{4} k b + \frac{2}{5} \varepsilon_1 - \frac{2}{5} \varepsilon_3 \right); \quad (23)$$

and similarly when the motion is parallel to the z -axis with uniform speed W , we have

$$u = W f_2(z, x, y, c, -\varepsilon_2, -\varepsilon_3) + W \phi_2(z, x, y, c), \quad (24)$$

$$v = W f_3(z, x, y, c, -\varepsilon_2, -\varepsilon_3) + W \phi_3(z, x, y, c), \quad (25)$$

$$w = W f_1(z, x, y, c, -\varepsilon_2, -\varepsilon_3) + W \phi_1(z, x, y, c), \quad (26)$$

and

$$F_z = -6 \pi \mu W c \left(1 + \frac{3}{4} k c + \frac{2}{5} \varepsilon_2 + \frac{2}{5} \varepsilon_3 \right). \quad (27)$$

In general, when the solid is moving in any direction with a uniform velocity whose components parallel to the x -, y - and z -axes are U , V , W respectively, the fluid motion can be obtained, upto this approximation, by superposing (that is, by adding the corresponding expressions for) the values of u , v , w in the three cases given above. And the formulas (19), (23) and (27) will denote the components of the resistance of the ellipsoid.

By repeating the process indicated above and retaining the terms of the second (or higher) degrees in the ε 's or in ka , we can obtain results upto any desired degree of approximation, only that we have to add a number of terms at every step and thus make the

calculations more elaborate. Symbolically, we can summarise the process thus:

Let

$$\left. \begin{aligned} u &= u_0 + u_1 + u_2 + \dots \\ v &= v_0 + v_1 + v_2 + \dots \\ w &= w_0 + w_1 + w_2 + \dots \\ p &= p_0 + p_1 + p_2 + \dots \end{aligned} \right\} \quad . \quad . \quad . \quad . \quad . \quad (28)$$

where u_0, v_0, w_0, p_0 stand for the corresponding values for the sphere of radius a ; u_1, v_1, w_1, p_1 are additional terms of the first degree for the ellipsoid, and u_2, v_2, w_2, p_2 those of the second degree, etc., in the ε 's and in k (if necessary). The number of terms on the right-hand side is always finite since they are being added one by one. The conditions to be satisfied are:

- $$\left. \begin{aligned} (i) & \text{ the equations of motion;} \\ (ii) & u = U, v = V, w = W, \text{ on the ellipsoid;} \\ (iii) & u = 0, v = 0, w = 0, \text{ at infinity.} \end{aligned} \right\} \quad . \quad . \quad . \quad (10A)$$

As u_0, v_0, w_0 already satisfy the above conditions, and as the additional terms are added step by step, we see that the conditions (ii) and (iii) are to be replaced by

- $$\left. \begin{aligned} (ii) & u_n = 0, v_n = 0, w_n = 0 \text{ on the ellipsoid, } n=1, 2, 3 \dots \\ (iii) & u_n = 0, v_n = 0, w_n = 0 \text{ at infinity, } n=1, 2, 3 \dots \end{aligned} \right\} \quad (10B)$$

The equation of continuity leads to

$$\frac{\partial}{\partial x}(u_n) + \frac{\partial}{\partial y}(v_n) + \frac{\partial}{\partial z}(w_n) = 0; \quad (29)$$

and the other equations of motion can be suitably modified for simplification at every stage. The equation to the ellipsoid is to be put as

$$\rho = a + F_1 + F_2 + \dots \quad . \quad . \quad . \quad . \quad . \quad (30)$$

THE RECESSION OF THE SPIRAL NEBULAE

BY

K. V. SASTRY, M. Sc. (Benares)

(Communicated by Prof. V. V. Narlikar)

The spiral nebulae recede according to the law,

$$\frac{\dot{x}}{x} = \frac{\dot{y}}{y} = \frac{\dot{z}}{z} = \frac{1}{t} \dots \dots \dots (1)$$

Prof. Narlikar* has already shown that this law is the only set of relations between the position, time and velocity of a nebula which remains invariant for the Lorentz transformation. We examine in this note the nature of transformations for which (1) remains invariant. Let us consider the transformation,

$$x' = f_1(x, y, z, t), \quad y' = f_2(x, y, z, t), \quad z' = f_3(x, y, z, t) \quad \text{and} \quad t' = f_4(x, y, z, t) \dots \dots \dots (2)$$

Let us suppose that this transformation yields

$$x'/x' = y'/y' = z'/z' = 1/t' \quad \text{from (1). Then}$$

$$\begin{aligned} \frac{1}{f_4} &= \frac{\frac{\partial f_1}{\partial x} \dot{x} + \frac{\partial f_1}{\partial y} \dot{y} + \frac{\partial f_1}{\partial z} \dot{z} + \frac{\partial f_1}{\partial t}}{\frac{\partial f_4}{\partial x} \dot{x} + \frac{\partial f_4}{\partial y} \dot{y} + \frac{\partial f_4}{\partial z} \dot{z} + \frac{\partial f_4}{\partial t}} \\ &= \frac{x \frac{\partial f_1}{\partial x} + y \frac{\partial f_1}{\partial y} + z \frac{\partial f_1}{\partial z} + t \frac{\partial f_1}{\partial t}}{x_x \frac{\partial f_4}{\partial x} + y \frac{\partial f_4}{\partial y} + z \frac{\partial f_4}{\partial z} + t \frac{\partial f_4}{\partial t}} \dots \dots \dots (3) \end{aligned}$$

It is clear from (3) that if f_1, f_2, f_3, f_4 are homogeneous polynomials in (x, y, z, t) then the degree of each polynomial must be the same, say, n .

Further if x, y, z, t , are expressed in terms of x', y', z', t' then by the extended principle of relativity, x, y, z, t , each must be a polynomial of degree n in x', y', z', t' , which will be possible only if $n=1$. Hence any linear transformation between x, y, z, t and x', y', z', t' , not necessarily of the Lorentz type, leaves the law of recession invariant. This can also be easily verified.

* *Nature*, Jan. 26, 1935, p. 149.

The preceding argument can be generalized to include the solutions where f_1, f_2, f_3, f_4 are not necessarily polynomials but homogeneous functions to which Euler's theorem of differentiation becomes applicable. It is really the postulated invariance of the form of the transformation that gives us the linearity.

If no assumption is made about the forms of f_1 and f_4 one obtains from (3) that $\log (f_1 / f_4)$ must satisfy the differential equation

$$x \frac{\partial \phi}{\partial x} + y \frac{\partial \phi}{\partial y} + z \frac{\partial \phi}{\partial z} + t \frac{\partial \phi}{\partial t} = 0$$

the possibility of ϕ being a homogeneous function of x, y, z, t has already been considered. Suppose now that ϕ is a function of r and t so that

$$r \frac{\partial \phi}{\partial r} + t \frac{\partial \phi}{\partial t} = 0$$

giving $f_1 / f_4 = e^{\psi(r/t)}$, where ψ is any function.

Thus the invariance holds good also for transformations of the form

$$x' = t' e^{\psi_1(r/t)}, \quad y' = t' e^{\psi_2(r/t)}, \quad z' = t' e^{\psi_3(r/t)}.$$

A NOTE ON THE UNDISTURBED PLANETARY MOTION

BY

D. R. SHARMA, M.Sc. (Benares).

(Communicated by Prof. V. V. Narlikar)

We derive in this paper certain properties of the undisturbed planetary motion about the sun. The properties are perhaps trivial but probably of sufficient interest to be placed on record.

Taking a set of rectangular axes in the plane of the motion let us denote by (x_1, o) the position of the sun at any instant t , the position of the planet by (x, y) and its velocity relative to the sun by (u, v) . If (x_0, o) is the centre of the ellipse at time t we have in the usual notation,

$$x_1 - x_0 = ae, \quad (1)$$

$$x - x_0 = a \cos \Theta, \quad (2)$$

$$y = a (1 - e^2)^{\frac{1}{2}} \sin \Theta, \quad (3)$$

$$u = -(\mu/a)^{\frac{1}{2}} \sin \Theta / (1 - e \cos \Theta), \quad (4)$$

$$v = (\mu/a)^{\frac{1}{2}} (1 - e^2)^{\frac{1}{2}} \cos \Theta / (1 - e \cos \Theta), \quad (5)$$

Θ being eccentric anomaly, Choosing any origin and substituting $u = \lambda X$ and $v = \lambda Y$ where X and Y are rectangular co-ordinates we find on eliminating Θ from (4) and (5)

$$X^2 + (Y - K \tan \phi / \lambda)^2 = K^2 \sec^2 \phi / \lambda^2, \quad \dots (6)$$

where $\sin \phi = e$ and $K = \sqrt{\mu/a}$.

Eliminating Θ and e successively from (3), (4) and (5) we obtain

$$a = \frac{uy}{v} \frac{\left\{ (x_1 - x)^2 + y^2 \right\}^{\frac{1}{2}} \left\{ x_1 - x + \frac{uy}{v} \right\}}{\left\{ (x_1 - x + \frac{uy}{v})^2 - (x_1 - x)^2 - y^2 \right\}} \quad (7)$$

Similarly, from (1), (2) and (7),

$$e = \frac{(x_1 - x - vy/u)}{\left\{ y^2 + (x_1 - x)^2 \right\}^{\frac{1}{2}}} \quad (8)$$

$$\text{Also } \mu = \frac{uv}{y} (x_1 - x + uy/v) \left[y^2 + (x_1 - x)^2 \right]^{\frac{1}{2}} \dots (9)$$

From (7), (8) and (9) we can obtain expressions for the period T of the motion, the area of the ellipse and the constant of angular momentum. Thus we obtain the exact relations between the constants a, e, μ of the motion and the co-ordinates and the relative velocity at any instant of the motion.

A SIMPLIFICATION OF EINSTEIN'S EQUATIONS.

By

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INTRODUCTION.

In the following we are concerned only with those solutions of the relativistic equations of gravitation which are associated with a line-element of the form

$$ds^2 = -\theta_1^2 dx_1^2 - \theta_2^2 dx_2^2 - \theta_3^2 dx_3^2 + \theta_4^2 dx_4^2 \dots \dots \dots \quad (1)$$

where $\theta = \theta(x_1, x_2, x_3, x_4)$. This form has been found out to be very useful in most of the relativistic discussions of problems of cosmogony and is, therefore, chosen here as the subject of discussion. It is obvious that some of the well-known solutions of Einstein's gravitational equations are particular cases of the form (i): Lemaître's and Schwarzschild's may be quoted as particular cases. To proceed with the discussion any assumption that is made about the energy tensor must be clearly set out. A perfectly general energy tensor would naturally mean a perfectly general distribution of matter the exploration of which would be beyond our mathematical reach. A vast number of discussions have already been made with certain restricted assumptions about the distribution of matter in the field. We assume here as in several cognate discussions, that there is no flux of matter outward or inward, and that only the four principal components of the energy tensor, $T_{\mu r}$, are therefore non-zero.

One* of us has already shown elsewhere that the relativity equations to be solved for the form (1) can be put in a strikingly neat form involving Laplacian operators of the first and the second kind. The ten components of the contracted Riemann-Christoffel Tensor $G_{\mu, \nu}$ furnish us with the ten gravitational equations; only six of these are independent, in general, owing to the four well-known identities. It is possible that, under certain circumstances, the six equations which involve the six non-principal components of the tensor $G_{\mu, \nu}$ are all independent. In our case these six equations are the simplest as we have assumed that only the principal components of $T_{\mu, \nu}$ are

* "Relativity & Cosmogony", lectures given by V. V. Narlikar before the University of Bombay, Jan. 1933, Bombay University Journal, 1933.

non-zero. In this paper we, therefore, consider only these six equations and devise a method to tackle them. In case these six equations are all independent the remaining four may be said to define the components of the energy tensor, when this is not so one or more of the principal equations must be solved before the field can be explored. All considerations about the four principal equations have however, been postponed to the second paper.

The very form in which the six equations appear here enables us to split each of them into two for the sake of investigation. We deal here with these twelve equations, get some of their solutions, and indicate their geometrical significance. The new solutions thus derived are not all abstract: some of them, at least, should attract attention from the physical point of view as the most prominent solutions of Einstein's equations for gravitation are found to be particular members of this set of solutions.

THE EQUATIONS OF GRAVITATION

It is well-known that in the usual notation of relativity the tensor $G_{\mu\nu}$ is given by

$$G_{\mu\nu} = -\frac{\partial}{\partial x^\alpha} \{ \mu \gamma, \alpha \} + \{ \mu \alpha, \beta \} \{ \gamma \beta, \alpha \} + \frac{\partial^2}{\partial x^\mu \partial x^\nu} \log \sqrt{-g} - \{ \mu \gamma, \alpha \} \frac{\partial}{\partial x^\alpha} \log \sqrt{-g} \dots (2)$$

For the form (i) $x^1 = x_1, x^2 = x_2, x^3 = x_3, x^4 = x_4$ and $g_{11} = -\theta^2$,

$g_{22} = -\theta^2_2, g_{33} = -\theta^2_3, g_{44} = \theta^2_4$ while $g_{\mu\gamma} = 0, \mu \neq \gamma$.

Substituting these in (2) we have

$$\begin{aligned} G_{11} = & -\frac{\partial}{\partial x_1} \{ 11, 1 \} - \frac{\partial}{\partial x_2} \{ 11, 2 \} - \frac{\partial}{\partial x_3} \{ 11, 3 \} - \frac{\partial}{\partial x_4} \{ 11, 4 \} + \{ 11, 1 \} \\ & \{ 11, 1 \} + \{ 11, 2 \} \{ 12, 1 \} + \{ 11, 3 \} \{ 13, 1 \} + \{ 11, 4 \} \{ 14, 1 \} + \{ 12, 1 \} \\ & \{ 11, 2 \} + \{ 12, 2 \} \{ 12, 2 \} + \{ 12, 3 \} \{ 13, 2 \} + \{ 12, 4 \} \{ 14, 2 \} + \{ 13, 1 \} \\ & \{ 11, 3 \} + \{ 13, 2 \} \{ 12, 3 \} + \{ 13, 3 \} \{ 13, 3 \} + \{ 13, 4 \} \{ 14, 3 \} + \{ 14, 1 \} \\ & \{ 11, 4 \} + \{ 14, 2 \} \{ 12, 4 \} + \{ 14, 3 \} \{ 13, 4 \} + \{ 14, 4 \} \{ 14, 4 \} + \frac{\partial^2}{\partial x_1^2} \\ & \log (\theta_1 \theta_2 \theta_3 \theta_4) - \left[\{ 11, 1 \} \frac{\partial}{\partial x_1} + \{ 11, 2 \} \frac{\partial}{\partial x_2} + \{ 11, 3 \} \frac{\partial}{\partial x_3} + \right. \\ & \left. \{ 11, 4 \} \frac{\partial}{\partial x_4} \right] \log (\theta_1 \theta_2 \theta_3 \theta_4) = \frac{1}{\theta_2} \frac{\partial^2 \theta_2}{\partial x_1^2} + \frac{1}{\theta_3} \frac{\partial^2 \theta_3}{\partial x_1^2} + \frac{1}{\theta_4} \frac{\partial^2 \theta_4}{\partial x_1^2} - \\ & \frac{1}{\theta_1 \theta_2} \frac{\partial \theta_1}{\partial x_1} \frac{\partial \theta_2}{\partial x_1} - \frac{1}{\theta_1 \theta_3} \frac{\partial \theta_1}{\partial x_1} \frac{\partial \theta_3}{\partial x_1} - \frac{1}{\theta_1 \theta_4} \frac{\partial \theta_1}{\partial x_1} \frac{\partial \theta_4}{\partial x_1} + \frac{\theta_1}{\theta_2 \theta_3 \theta_4} \left\{ \frac{\partial}{\partial x_2} \right. \\ & \left. \left(\frac{\theta_3 \theta_4}{\theta_2} \frac{\partial \theta_1}{\partial x_2} \right) + \frac{\partial}{\partial x_3} \left(\frac{\theta_2 \theta_4}{\theta_3} \frac{\partial \theta_1}{\partial x_3} \right) + \frac{\partial}{\partial x_4} \left(\frac{\theta_2 \theta_3}{\theta_4} \frac{\partial \theta_1}{\partial x_4} \right) \right\} \end{aligned}$$

$$\begin{aligned}
&= \theta_1^2 \left[\frac{1}{\theta_2} \frac{\partial^2 \theta_2}{\partial X_1^2} + \frac{1}{\theta_3} \frac{\partial^2 \theta_3}{\partial X_1^2} + \frac{1}{\theta_4} \frac{\partial^2 \theta_4}{\partial X_1^2} \right] + \theta_1 \nabla_1^2 \theta_1 \\
&= \theta_1^2 \left[\frac{\nabla_1^2 \theta_1}{\theta_1} + \frac{1}{\theta_2} \frac{\partial^2 \theta_2}{\partial X_1^2} + \frac{1}{\theta_3} \frac{\partial^2 \theta_3}{\partial X_1^2} + \frac{1}{\theta_4} \frac{\partial^2 \theta_4}{\partial X_1^2} \right] \dots \dots \dots (3)
\end{aligned}$$

where $\frac{\partial}{\partial X_1} = \frac{1}{\theta_1} \frac{\partial}{\partial x_1}$ and ∇_1^2 is the well-known Laplacian

operator for $\theta_2^2 \propto x_2^2 + \theta_3^2 \propto x_3^2 + \theta_4^2 \propto x_4^2$. We can write similarly,

$$G_{22} = \theta_2^2 \left[\frac{\nabla_2^2 \theta_2}{\theta_2} + \frac{1}{\theta_1} \frac{\partial^2 \theta_1}{\partial X_2^2} + \frac{1}{\theta_3} \frac{\partial^2 \theta_3}{\partial X_2^2} + \frac{1}{\theta_4} \frac{\partial^2 \theta_4}{\partial X_2^2} \right]$$

$$G_{33} = \theta_3^2 \left[\frac{\nabla_3^2 \theta_3}{\theta_3} + \frac{1}{\theta_1} \frac{\partial^2 \theta_1}{\partial X_3^2} + \frac{1}{\theta_2} \frac{\partial^2 \theta_2}{\partial X_3^2} + \frac{1}{\theta_4} \frac{\partial^2 \theta_4}{\partial X_3^2} \right]$$

while G_{44} differs from G_{11} , G_{22} , G_{33} as is to be expected from (1) so that

$$G_{44} = \theta_4^2 \left[-\frac{\nabla_4^2 \theta_4}{\theta_4} + \frac{1}{\theta_1} \frac{\partial^2 \theta_1}{\partial X_4^2} + \frac{1}{\theta_2} \frac{\partial^2 \theta_2}{\partial X_4^2} + \frac{1}{\theta_3} \frac{\partial^2 \theta_3}{\partial X_4^2} \right]$$

Similarly calculations may be made for the non-principal components of $G_{\mu\nu}$ for which μ is not equal to ν . Let us take for example G_{12} which reduces to

$$\begin{aligned}
&\frac{1}{\theta_3} \frac{\partial^2 \theta_3}{\partial x_1 \partial x_2} + \frac{1}{\theta_4} \frac{\partial^2 \theta_4}{\partial x_1 \partial x_2} - \frac{1}{\theta_1 \theta_3} \frac{\partial \theta_1}{\partial x_2} \frac{\partial \theta_3}{\partial x_1} - \frac{1}{\theta_1 \theta_4} \frac{\partial \theta_1}{\partial x_2} \frac{\partial \theta_4}{\partial x_1} \\
&- \frac{1}{\theta_2 \theta_3} \frac{\partial \theta_2}{\partial x_1} \frac{\partial \theta_3}{\partial x_2} - \frac{1}{\theta_2 \theta_4} \frac{\partial \theta_2}{\partial x_1} \frac{\partial \theta_4}{\partial x_2}
\end{aligned}$$

$$\begin{aligned}
\text{Thus } G_{12} &= \frac{1}{\theta_3} \left[\left\{ \frac{\partial^2}{\partial x_1 \partial x_2} - \frac{\partial \log \sqrt{\theta_1^2}}{\partial x_2} \frac{\partial}{\partial x_1} - \frac{\partial \log \sqrt{\theta_2^2}}{\partial x_1} \frac{\partial}{\partial x_2} \right\} \theta_3 \right] \\
&\quad \frac{1}{\theta_4} \left[\left\{ \frac{\partial^2}{\partial x_1 \partial x_2} - \frac{\partial \log \sqrt{\theta_1^2}}{\partial x_2} \frac{\partial}{\partial x_1} - \frac{\partial \log \sqrt{\theta_2^2}}{\partial x_1} \frac{\partial}{\partial x_2} \right\} \theta_4 \right] \\
&= \frac{\nabla_{12} \theta_3}{\theta_3} + \frac{\nabla_{12} \theta_4}{\theta_4}
\end{aligned}$$

which defines the Laplacian operator, ∇_{12} of the second kind. If we define similarly ∇_{23} , ∇_{34} , etc. We have,

$$G_{23} = \frac{\nabla_{23} \theta_1}{\theta_1} + \frac{\nabla_{23} \theta_4}{\theta_4}$$

$$G_{34} = \frac{\nabla_{34} \theta_1}{\theta_1} + \frac{\nabla_{34} \theta_2}{\theta_2}, \text{ etc.}$$

The gravitational equations are

$$G_{\mu\nu} - \lambda g_{\mu\nu} = -k \left(T_{\mu\nu} - \frac{1}{2} T g_{\mu\nu} \right) \dots \dots \dots (4)$$

in the usual notation. The six non-principal equations with which we are concerned here are

$$\left. \begin{aligned}
&\frac{\nabla_{12} \theta_3}{\theta_3} + \frac{\nabla_{12} \theta_4}{\theta_4} = 0 \\
&\frac{\nabla_{23} \theta_1}{\theta_1} + \frac{\nabla_{23} \theta_4}{\theta_4} = 0 \text{ etc.}
\end{aligned} \right\} \dots \dots \dots (5)$$

(3) and (5) yield us standard results for the form (1) so that whenever a line-element which is a particular case of (1) comes up for discussion the corresponding relativity equations can be written down straightway without any preliminary tedious calculations such as those of the Christoffel symbols being done.

THE SOLUTION OF $s+ap+bq+cz=o$

Let us consider now the solution of the differential equation

$$s+ap+bq+cz=o$$

$$\text{or } \frac{\partial^2 z}{\partial x \partial y} + a \frac{\partial z}{\partial x} + b \frac{\partial z}{\partial y} + cz = o \dots\dots\dots (6)$$

where a, b and c are functions of x and y . We may write

$$(6) \text{ either as } \frac{\partial}{\partial x} \left(\frac{\partial z}{\partial y} + az \right) + b \left(\frac{\partial z}{\partial y} + az \right) - hz = o \dots (7)$$

$$\text{or as } \frac{\partial}{\partial y} \left(\frac{\partial z}{\partial x} + bz \right) + a \left(\frac{\partial z}{\partial x} + bz \right) - kz = o \dots (8)$$

$$\text{where } h = \frac{\partial a}{\partial x} + ab - c, \quad k = \frac{\partial b}{\partial y} + ab - c \dots\dots\dots (9)$$

h and k are known as the invariants of the differential equation (6), If $h = o$

$$\begin{aligned} \frac{\partial z}{\partial y} + az &= Y e^{-\int b dx} \\ \text{or } z e^{\int a dy} &= \int Y e^{\int a dy} \int b dx \\ \text{or } Z &= X e^{-\int a dy} + e^{\int a dy} \int X' e^{\int b dx} dy \dots \end{aligned} \quad (10)$$

where X and Y are arbitrary functions of x and y respectively.

Similarly if $k = o$

$$Z = Y' e^{-\int b dx} + e^{\int b dx} \int X' e^{\int a dy} dx \dots \quad (11)$$

where X' and Y' are arbitrary functions of x and y respectively. We will now proceed to use the results (10) and (11) to solve the equations (5).

$$\text{The Equation } \frac{\Delta_{12}\theta_3}{\theta_3} + \frac{\Delta_{12}\theta_4}{\theta_4} = 0$$

To solve this equation we first split it into two viz.,

$$\frac{\Delta_{12}\theta_3}{\theta_3} = -C, \quad \frac{\Delta_{12}\theta_4}{\theta_4} = C \dots\dots\dots (12)$$

C may be any function of the four variables and it will be determined later on. The two invariants for the first equation in (12) are

$$h = \frac{\partial a}{\partial x} + ab - C$$

$$k = \frac{\partial b}{\partial y} + ab - C$$

and for the second equation in (12)

$$h' = \frac{\partial a}{\partial x} + ab + C$$

$$k' = \frac{\partial b}{\partial y} + ab + C$$

where $a = -\frac{\partial u}{\partial y}$, $b = -\frac{\partial v}{\partial x}$, $u = \log \theta_1$ and

$v = \log \theta_2$. If $h = 0$, $k' = 0$ we get a solution which is of the same form as the solution when $k = 0$, $h' = 0$. If $h = 0$ and $h' = 0$ simultaneously we get $c = 0$. Consideration of this and the other case $k = 0$, $k' = 0$ which also leads to $C = 0$ gives comparatively trivial results. If $h = 0$, $k' = 0$

$$\frac{\partial a}{\partial x} + \frac{\partial b}{\partial y} + 2ab = 0 \quad (13)$$

$$\frac{\partial a}{\partial x} - \frac{\partial b}{\partial y} = 2c \quad (14)$$

The equations (13) and 14 reduce to

$$\frac{\partial^2 u}{\partial x_1 \partial x_2} + \frac{\partial^2 v}{\partial x_1 \partial x_2} = 2 \frac{\partial u}{\partial x_2} \cdot \frac{\partial v}{\partial x_1} \dots \dots \dots (15)$$

$$\frac{\partial^2 v}{\partial x_1 \partial x_2} - \frac{\partial^2 u}{\partial x_1 \partial x_2} = 2c \dots \dots \dots (16)$$

The solution of (16) is obviously given by

$$\log \frac{\theta_2}{\theta_1} = \int \int 2c \, dx_1 \, dx_2 + Z_{134} \times Z_{234} \dots \dots \dots (17)$$

Z_{134} is an arbitrary function of x_1, x_3, x_4 and Z_{234} of x_2, x_3, x_4 . To solve (15) assume $\frac{\partial u}{\partial x_2} = \phi$ which reduces the equation

$$\text{to } \frac{\partial \phi}{\partial x_1} + \frac{\partial \phi}{\partial x_2} + 2\phi\phi = 0 \dots \dots \dots (18)$$

where $\frac{\partial v}{\partial x_1} = \psi$ Hence

$$\psi - \int 2\phi \, dx_2 - \int \frac{\partial \phi}{\partial x_1} \, dx_2 = \int 2\phi \, dx_2 + \gamma_{134}$$

$$\psi = \frac{\partial v}{\partial x_1} - \gamma_{134} e^{\int 2\phi \, dx_2} \int 2\phi \, dx_2 \int \frac{\partial \phi}{\partial x_1} \, dx_2 - \int 2\phi \, dx_2$$

$$= \gamma_{134} e^{2u} - \frac{2u}{e} \int \frac{\partial^2 u}{\partial x_1 \partial x_2} e^{2u} \, dx_2$$

$$v = \int \gamma_{134} \frac{\partial^2 u}{\partial x_1 \partial x_2} dx_1 - \int \frac{\partial^2 u}{\partial x_1 \partial x_2} \gamma_{234} dx_2 dx_1 + \gamma_{234} \quad (19)$$

$$\text{or } \log \theta_2 = \int \gamma_{134} \theta_1^2 dx_1 - \int \theta_1^2 \int \frac{\partial_2 \log \theta_1}{\theta_1^2 \partial x_1 \partial x_2} dx_2 dx_1 + \gamma_{234}. \quad (20)$$

Here γ_{134} and γ_{234} have the same meaning as Z_{134} Z_{234} . Thus (17) and (20) together constitute the result of the condition which we have found necessary for solving the equations (12).

We may now write the solutions of the equations (12) by making use of the result (10) and (11).

$$\theta_3 = X_{134} \theta_1 + \theta_1 \int X_{234} \frac{\partial_2}{\theta_1} dx_2 \dots \dots \dots \quad (21)$$

$$\theta_4 = X'_{234} \theta_2 + \theta_2 \int X'_{134} \frac{\partial_1}{\theta_2} dx_2 \dots \dots \dots \quad (22)$$

where X'_{134} is some function of x_1, x_3, x_4 , Similarly for X_{234}' X'_{234} etc. As yet X_{134} γ_{234} are all arbitrary. (17), (20), (21) and (22) constitute the result of our investigation of one of the six equations (5).

Treating all the six equations in a similar manner we will get twenty-four conditions connecting θ_1 θ_2 θ_3 θ_4 . The problem next is to pick out the most general values of the θ s possible so as to be consistent with all the conditions.

Assuming that each of the four θ s is a product of functions of x_1, x_2, x_3, x_4 separately we get a series of solutions of which the most prominent are Lemaitre's nonstatic universe and Schwarzschild's solution for a particle.

The above mentioned two solutions satisfy the twelve equations $\nabla_{12} \theta_3 = \nabla_{12} \theta_4 = 0$, $\nabla_{13} \theta_2 = \nabla_{13} \theta_4 = 0$ etc. These twelve equations suggest a geometrical relationship between $\theta_1, \theta_2, \theta_3$ and θ_4 ; for each of the equations is of the form

$$\frac{\partial^2 \phi}{\partial u \partial v} - \frac{\partial \log \sqrt{E}}{\partial v} \frac{\partial \phi}{\partial u} - \frac{\partial \log \sqrt{F}}{\partial u} \frac{\partial \phi}{\partial v} = 0$$

which is satisfied by the rectangular co-ordinates of a point on the surface on which $U = \text{constant}$ and $V = \text{const.}$ are lines of curvature.

SUMMARY

The line element $ds^2 = -\theta_1^2 dx^2 - \theta_2^2 dy^2 - \theta_3^2 dz^2 + \theta_4^2 dt^2$ is discussed taking each θ to be a function of x, y, z, t . Some new solutions are obtained.

TRANSMISSION OF VISIBLE LIGHT THROUGH ARTIFICIAL HOMOGENEOUS CLOUDS

BY

G. R. PARANJPE and N. N. BHAGVAT

INTRODUCTION

The transmission of visible light through fog has been the object of investigation during the last thirty years on account of the increasing application of aviation to commerce. Much of the experimental data on this problem are, however, purely qualitative and the quantitative data that are available admit of little analysis or mutual comparison, each worker having his own conditions of experiment, differing from those of the rest.

Previous work :—

The problem has been studied by Rudolph¹, Haecker², Utterback³, Werner⁴, Granath and Hulburt⁵, Anderson⁶, Houghton⁷, Külb⁸, and Kobayasi and Nukiyama⁹.

The works of Haecker (1905) and Utterback (1919), dependent as they are on the sensitivity curve of the eye, are of little use for generalization. Werner (1923) studied the attenuation of visible light by artificial fog, but he was unable to discover any regularity in the transmission, depending either on the wave-length or the size of the drops. Rudolph (1904) found for natural fogs a feeble increase in absorption with increase in the wave-length in the visible region of the spectrum.

Granath and Hulburt (1929) have made their measurements on natural fogs, using a quartz-spectrograph and a recording densitometer, in the visible part of the spectrum. They also took some measurements in the infra-red region and found a small but gradual increase in transmission for wave-lengths from $\lambda = 4000\text{A.U.}$ to $\lambda = 7000\text{A.U.}$, from where onwards, the transmission remained the same to about $\lambda = 30000\text{A.U.}$

Substantial and detailed is the work of Anderson (1930). He studied artificial fog (water-fogs according to him) in a closed vessel. He was able to produce water-clouds wherein it appears that the sizes of the drops were considerable, but no definite information about the absolute sizes has been given. Moreover, he used hygroscopic nuclei (MgCl_2) to obtain these clouds, which cannot

strictly be regarded as pure water-clouds. In common with Granath and Hulburt, he finds a rise in the transmission towards the red end of the spectrum.

In his work on artificial clouds of water, produced by condensing low-pressure steam, Houghton (1931) found a definite maximum transmission for the wave-length 4900A.U. The total absence of any such maximum in the results of any other investigator led Houghton to believe that the size of the drops in a cloud was one of the controlling factors in the transmission of light. The drops in his clouds ranged between 2 to 3 microns in diameter, and according to him, his clouds must have differed in this respect from those of the other investigators. Since no other investigators have given the size of the drops in their clouds, artificial or natural, this point could not be cleared.

Külb (1931) has studied the problem in great detail but he could neither work on natural clouds on account of unfavourable climate, nor could he produce stable artificial clouds of water; he therefore, worked on artificial clouds obtained from SiCl_4 and NH_3 , TiCl_4 , NH_3 and HCl , etc. These clouds consisted of particles having for their diameter values ranging from 1.2μ to 2.1μ . With particles of this size, he got, for all the clouds he investigated, a maximum absorption for the wave-length 5500A.U. and a minimum absorption for a wave-length between 25000 and 30000A.U. He expected water-clouds also to give similar results, although it does not appear why water-clouds, which are essentially transparent liquid particles, should behave as opaque solid particles like those of NH_4Cl .

Kobayasi and Nukiyama (1932-33) have studied the transmission for clouds of ammonium chloride, water, and mixtures of water and ammonium chloride. For NH_4Cl -clouds they find a sharp maximum transmission for $\lambda = 4500\text{A.U.}$ and negligible transmission below $\lambda = 3100\text{A.U.}$ For water, they get a flat maximum at $\lambda = 3600\text{A.U.}$ and a sharp and much greater maximum at $\lambda = 4780\text{A.U.}$ Clouds of mixtures of NH_4Cl and water exhibit a maximum transmission at 4400A.U. In their study of clouds from incense etc., they get, in the transmission-wavelength curves, two maxima which they attribute to the complex nature of the combustion products.

Present work :—

Though a good deal of experimental work had been done and tentative empirical formulae put forth by some investigators

(Granath & Hulburt and Anderson, for instance, take $I = I_0 e^{-\left(a + \frac{b}{\lambda^4}\right)}$ as a modification of Rayleigh's inverse fourth power law), a strictly theoretical solution of the problem was not forthcoming till

Stratton & Houghton¹⁰ undertook to investigate the problem with a view to see if there was any theoretical justification for Houghton's singular result, viz. a maximum transmission for 4900A.U.

It is this work which has been a source of interest to the present authors and in fact forms the basis of this investigation.

As will be shown presently (p. 33) it is possible to express the transmission as a function of the size of the drops in a cloud and the wave-length under consideration. No workers, in the first place, experimented upon stable clouds of pure water and, in the second place, controlled the size of the drops in their clouds; in point of fact, they have not endeavoured to ascertain the sizes of the drops as they did not expect the transmission to depend on the size of the drops to any very great extent.

Experiments have been going on in this laboratory for the last few years and it has been possible to obtain very stable clouds of pure water-drops, the radii of which could be known and varied within wide limits (1 to 8 microns). The problem of transmission of various wave-lengths in the visible spectrum through clouds, wherein the size of the drops ranged within wide limits, was therefore taken up, and though such a work is generally of a qualitative nature, attempts were made to give it a quantitative significance.

Since the transmission of light depends on the refractive index of the liquid, other liquids have been studied with a view to see how the refractive index affects the transmission characteristics of the liquids and whether these liquids exhibit any similarity to water.

For the first time, thus have pure liquid-vapours been investigated and the effect of the size of the drops on the transmission studied with any degree of accuracy.

Method adopted:—

The clouds were produced in a closed flask by the usual adiabatic expansion method of condensing a saturated vapour. Incense-stick smoke (which consists of very fine particles) was used to provide the nuclei for condensation. The size of the drops was determined by the corona-ring method, which is by far the most suitable method available, and the transmission for different wave-lengths was obtained by employing a sensitive photo-cell in conjunction with a monochromator.

(II)

SOME THEORETICAL CONSIDERATIONS.

In order to see if there was any theoretical justification for Houghton's⁷ result, Stratton & Houghton¹⁰ undertook to treat this

problem theoretically, and following Mie¹¹, Debye¹², & Jobst¹³ in their method of attack in the case of a similar problem, viz. colours of colloidal solutions, they obtained for the transmission ratio :

$$T = e^{-2 \pi n a^2 z K}.$$

where T = the transmission ratio (ratio of the intensities of a constant beam of light after and before passing through the cloud.)

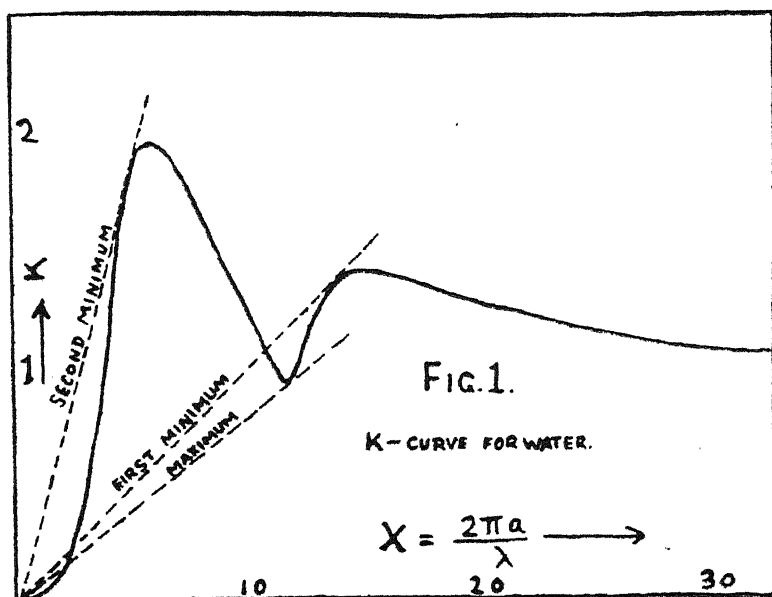
n = the number of drops per cc.,

a = the radius of the drops,

z = the length of the path of the beam through the cloud (the diameter of the flask),

$K = f(2 \pi a / \lambda)$, (where λ is the wave-length), depending on the refractive index of the liquid and therefore, characteristic of the liquid.

Stratton & Houghton have calculated the K -curve for water, It is given here in figure 1.



The above formula for the transmission ratio can be written as

$$T = e^{\frac{-AK}{a}}$$

where A is constant if the quantity of the liquid condensed per cc. is constant. It is to be seen how the nature of the K -curve affects the transmission, if this be plotted as a function of a .

Putting $\frac{K}{a} = y$, we get

$$T = e^{-Ay}$$

Differentiating with respect to a , and putting

$$\frac{dT}{da} = 0,$$

$$\frac{dT}{da} = -A \frac{dy}{da} e^{-Ay}$$

$$= -AT \frac{dy}{da} = 0.$$

$\therefore T$ is maximum or minimum when

$$\frac{dy}{da} = 0.$$

Now
$$\frac{dy}{da} = \frac{1}{a} \cdot \frac{dK}{da} - \frac{K}{a^2} = 0.$$

$$\therefore \frac{dK}{da} = \frac{K}{a}, \text{ for } T \text{ to be maximum or minimum.}$$

i. e., when $\lambda = \text{const.}$, $\frac{dK}{dx} \cdot \frac{\partial x}{\partial a} = \frac{K}{a}$, where $x = \frac{2\pi a}{\lambda}$,

i. e.
$$\frac{dK}{dx} = \frac{K}{x}.$$

Thus a maximum or a minimum for a given wavelength is given by the point of contact of the tangent from the origin to the K -curve (Fig. 1). Out of the three tangents that can be drawn from the origin to the curve $K = f(x)$, the two, corresponding to the maxima, give maximum values for K/a and therefore correspond to minimum transmission; while the third tangent corresponding to the intermediate minimum of the K -curve gives a minimum value for K/a and therefore corresponds to a maximum transmission.

If we denote by a_1, a_2, a_3 , the sizes of the drops for which these turning values occur, for any wave-length, we find that these sizes are given by the equation

$$a_m = \lambda x_m / 2\pi \dots\dots\dots (m = 1, 2, \& 3.),$$

where x_m has the three values corresponding to the three points of contact of the tangents from the origin to the K -curve. (Note:— $m = 1$ refers to the flat maximum of the K -curve; $m = 2$, to the minimum; and $m = 3$, to sharp maximum.)

$$\text{Hence } a_1 : a_2 : a_3 :: x_1 : x_2 : x_3 \dots\dots\dots (1),$$

for a particular wave-length.

From the graph of the K-curve for water (Fig. 1) we get the following values of x , for the turning points of the transmission curves :—

$$\begin{aligned} x_1 &= 14, \\ x_2 &= 12, \\ x_3 &= 5, \end{aligned} \quad \text{approximately,}$$

so that, $a_1 : a_2 : a_3 :: 1 : 0.86 : 0.36 \dots \dots \dots (1a)$, gives the ratio of the critical sizes of the drops for water.

If we consider the corresponding turning points of the transmission curves for different wave-lengths, we notice that for each of the above values of x we have

$$\frac{n a_m}{\lambda_n} = \frac{x_m}{2\pi} \quad \dots \dots \dots (n = 1, 2, 3, \dots \dots \dots) \\ (m = 1, 2, \& 3.)$$

where the suffix m refers to the turning point of the transmission curves and the prefix n refers to the wave-length. Thus $n a_m$ denotes the radius of drops for which the m th turning point of the transmission-curve corresponding to the wave-length λ_n occurs.

\therefore For a particular value of m ,

$$\frac{n a_m}{\lambda_n} = \text{constant} \dots \dots \dots (2).$$

This equation can be put in a convenient form as under :—

$$1^a m : 2^a m : 3^a m : \lambda_1 : \lambda_2 : \lambda_3 \dots \dots \dots (2a).$$

Thus the size of the drops for which the corresponding turning points of the transmission curves occur for different wave-lengths is proportional to the wave-length.

The ideal curves for transmission given in Fig. 2 on the next page, have been plotted from the equation

$$T = e^{-\frac{K}{a}}, \text{ where } a \text{ is expressed in } \mu.$$

This equation is obtained from Houghton's equation in the following way :—

We have

$$\begin{aligned} T &= e^{-2\pi n a^2 z K} \\ &= e^{-\frac{3}{2} \cdot \frac{4}{3} \pi a^3 n D \cdot \frac{z K}{D a}}, \end{aligned}$$

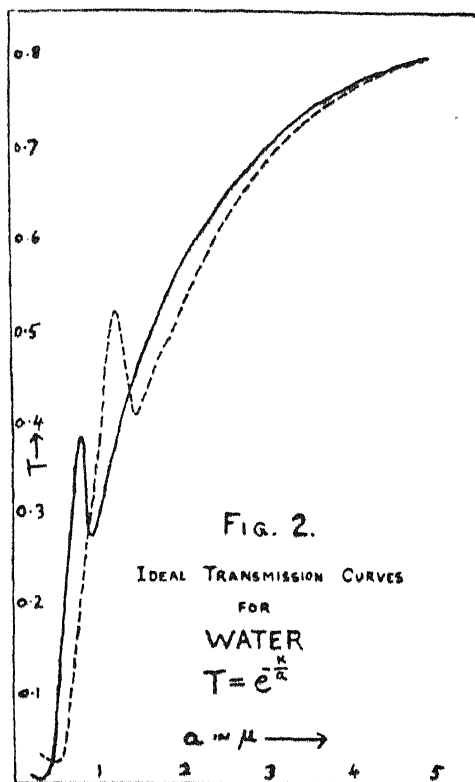
where, D = the density of the liquid = 1, here,

$$= e^{-\frac{3}{2} \cdot \frac{Q z K}{a}},$$

where $Q = \frac{4\pi a^3 n D}{3}$, the quantity of the liquid condensed per c.c.

Thus

$$T = e^{-\frac{K}{a}},$$



Full line for 4189 A. U. Dotted line for 6284 A.U.

if we put

$$\frac{3Qz}{2} = 1.$$

Since a has been expressed in μ , z must also be expressed in the same unit. When $z = 30$ cm. (the diameter of the flask in the present investigation), we therefore get

$$Q = \frac{2}{3z} = \frac{2}{3 \times 30 \times 10^4} = 2.22 \times 10^{-5} \text{ gm/cc.}$$

a value within the range of moderate expansion.

Since K is given as a function of $2\pi a/\lambda$, 6284 A.U. is a suitable wave-length in the red region for simplifying the calculations. The other wave-length is taken $\frac{2}{3}$ rds. of this, i.e., 4189 A.U.

The equation $x = \frac{2\pi a}{\lambda}$, now reduces to

$$x = 10a \quad \text{for } \lambda = 6284 \text{ A.U. and we get}$$

$$a_1 = 1.4\mu \text{ (first minimum),}$$

$$a_2 = 1.2\mu \text{ (maximum),}$$

$$a_3 = 0.5\mu \text{ (second minimum), for } \lambda = 6284 \text{ A.U. and}$$

$$\begin{aligned} a_1 &= 0.9 \mu ; \\ a_2 &= 0.8 \mu ; \\ a_3 &= 0.3 \mu ; \end{aligned} \quad \text{for } \lambda = 4189 \text{A.U.}$$

It is also evident from fig. 2 that for values of a greater than 5μ , both the wave-lengths have the same transmission.

The verification of the above results has been carried out by designing suitable experimental arrangements and it is this work which forms the subject matter of the present paper. The paper describes various arrangements

- (1) to keep the quantity of water condensed per cc. constant,
- (2) to obtain clouds, which, though individually uniform, consist of drops whose size varies considerably from cloud to cloud, and
- (3) to determine the size of the drops and the transmission of light of various wave-lengths through these clouds.

The transmission is then plotted as a function of the size of the drops in a cloud for each wave-length and these curves are compared with those given by the theory.

Before concluding these considerations however, it is to be remarked that the ideal curves do not point to the well-known law of the inverse fourth power of the wave-length when the values of a are small in comparison with the wave-length of light. It appears that this requires perfectly opaque particles, and the conclusion that Mecke¹⁴ has drawn about small drops that they do not behave as opaque discs seems to be justified.

III

EXPERIMENTAL ARRANGEMENTS AND GENERAL METHOD OF WORK.

Expansion Chamber :—

The arrangements were generally similar to those described before by Paranjpe, Mirchandani and Naik¹⁵. The flask, in which the clouds were produced, had a capacity of about 10 litres and was kept in an enclosure having four windows in its four sides. Two independent sources of light could thus be used, one for the determination of the size of the drops from the corona-ring measurements and the other to give the parallel beam of light required in the intensity determinations. An air-tight metal tank about four to five times larger than the flask was used for creating sudden expansion in the flask. The area of the bore of the tap connecting the tank and the flask was about one sq. cm. The pressures inside the tank and the flask could be read by means of two separate manometers.

The quantity of any liquid condensed as a result of an adiabatic expansion is a function of (1) the room temperature, (2) the atmospheric pressure, and (3) the final pressure in the flask after the expansion. In order, therefore, to keep the quantity of the condensed

liquid constant, all these three factors must be kept constant. This was achieved in the following way :—

For each set of experiment, the atmospheric pressure and the room temperature were observed, before and after, due care being taken to carry our experiments under as identical conditions as possible. The final pressure in the flask could be kept constant by putting the flask adiabatically in communication with the metal tank, wherein the pressure was brought down before each expansion to the same lower value by means of an exhaust pump.

The expansion could not be regarded as fully adiabatic but so long as the initial and final pressure in the flask remained the same in any expansion, the quantity of the liquid condensed would still remain the same, though it might not be equal to that calculated on the assumption of a full adiabatic expansion.

Measurement of the size of the drops :—

The size of the drops was determined by the usual corona-ring method. The source of light for the corona-rings was a 1000-watt electric lamp (lamp A) and the light of this lamp was brought to a focus at a distant point so that the beam of light incident on the flask could be regarded as parallel for most purposes.

The angular diameters of the corona-rings were measured by means of a theodolite. The distance at which the theodolite is kept from the flask is immaterial so far as the determination of the angular diameter of the corona-ring is concerned, since the angle subtended by a corona-ring is the same at all distances (if the beam of light is really parallel). This distance however sets a limit to the maximum angular diameter measurable (which is in fact equal to the angle subtended by the diameter of the flask at the theodolite). In order therefore to be able to measure large rings the theodolite was kept inside the enclosure very near to the flask. The rings measured in this manner are due to rays less divergent than those responsible for the same rings when the theodolite is kept at a distance; for when the theodolite is close to the flask it is directed to particles nearer to the centre of the flask. In fig. 3, the circle represents the flask and O, O' represent two positions of the theodolite.

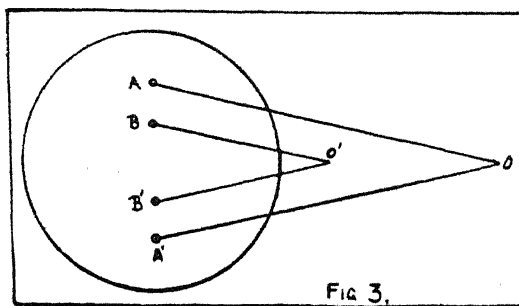


FIG 3.

When the theodolite is kept at O, the ring is due to drops, A, A'. When the theodolite is brought at O' nearer to the flask, the same ring is due to drops B, B'. Thus the ring in the latter case is due to rays nearer to the axis and therefore less divergent. The same thing will be also evident from the following note:—

A note on the verification of Stokes' law:—

Paranjpe, Mirchandani and Naik¹⁵ determined the size of the drops from that of the corona-ring and obtained the velocity of fall of the cloud by noting the time taken by the well defined top of the cloud to move down a known distance. Their results give a mean value of 2.04 for V'/V , where V' represents the velocity calculated from Stokes' law for the particular size of the drops, and V the observed velocity. This deviation from the law was attributed to the mutual influence of the drops and the influence of the sides of the vessel.

Since V as well as V' is proportional to the square root of the radius of the drops, the value of the radius obtained from the ring measurements was about 1.4 times that obtained from Stoke's law. This discrepancy occurred invariably when the theodolite was kept at a distance of about a metre or so from the flask. But on removing the theodolite nearer to the flask this ratio ultimately reduced to about 1.1, the ring measurements being more accurate, as the rings were now due to rays nearer to the axis (and therefore less divergent.)

A rough idea about the closeness with which the particles were packed together in these clouds can be obtained from the following simple calculations:—

If there be n drops per cc., each of volume v , and if Q be the quantity of water condensed per cc. we have

$$(D) \quad nv = Q, \quad D = \text{the density} = 1, \text{ here,}$$

and $nV = 1$, where V is the space occupied (not filled) by each drop.

$$\therefore \frac{V}{v} = \frac{1}{Q}.$$

Since Q never exceeded 5×10^{-6} gm/cc. in these experiments, even on the assumption of a full adiabatic expansion, the least value of

$$\frac{V}{v} = \frac{10^6}{5} = 2 \times 10^5,$$

Or, if we want the ratio $\frac{d}{a}$, where d is the distance between the centres of the drops and their radius, we have

$$(D) \frac{4 \pi a^3 n}{3} = Q$$

$$\text{and} \quad d^3 n = 1$$

$$\therefore \frac{d^3}{a^3} = \frac{4 \pi}{3Q} = \frac{4 \pi \cdot 10^6}{3 \cdot 5}$$

$$\text{i. e.} \quad \frac{d}{a} = \left(\frac{88}{105} \right)^{\frac{1}{3}} \times 100 = 95 \text{ (approx.)}$$

It is thus seen that the drops were so far apart as not to be able to exert any influence on the surrounding drops. The slightly low value of the observed velocity of fall was due to the sides of the flask. The cloud, when falling, moved faster in the centre than at the edge, as was evident from the slight depression in the middle of the cloud. It was not possible to measure the velocity of this central part and one had to be content with the measurement of the velocity at the edge.

A further improvement in the measurement of the angular diameter of the rings was made by attaching a pointer to the theodolite. This pointer was fixed into the tube for the base-scale eyepiece and rested on the moveable disc of the theodolite and was carried along with it by a screw projecting upwards from it, when it was turned one way; and when the disc was turned the other way, the pointer remained in its extreme position and the disc turned alone. By this self-recording arrangement quick measurements were rendered possible.

When observed through a coloured glass filter, bright diffraction rings appear separated by dark ones. The larger the dark ring thus observed the greater is its width and the dimmer it becomes. The present measurements were, therefore, made with blue rings without using any coloured glass filter. Consequently, the size of the drops was determined from the following formula corresponding to a maximum intensity (Humphrey's Physics of the Air, page 528) :—

$$\sin \theta = \frac{m \lambda}{2 \pi a} \quad \text{where,}$$

θ = angle subtended by the radius of the corona-ring at the eye of the observer,

λ = mean wave-length of light forming the corona-ring,

a = average radius of the drops.

Since the first blue ring was always observed the value of $\frac{m}{\pi}$ was

taken to be 0.819 which corresponds to the first maximum. The average wave-length was taken to be 4600A.U.

The appearance of corona-rings is evidently an indication that the clouds consist of uniform droplets. Further, the following method was adopted in obtaining clouds, having drops of different sizes :—

A certain number of nuclei was once for all introduced into the flask. Condensation did not take place on all the nuclei but only on a fraction (perhaps a definite fraction) of the available nuclei. As the cloud settled, some of the nuclei went down into the liquid and the number of available nuclei thus decreased. As a result of this, at each successive expansion the size of the drops became greater and greater since the number of nuclei went on decreasing while the quantity of liquid condensed remained the same.

The extent to which the radii of the drops could be measured ranged from 1 to 8 microns.

According to Mecke¹⁴, the formula for the determination of the size of the drops from the corona-measurements does not hold good for drops less than 4μ in radius; the smaller drops do not behave as opaque circular discs and therefore the refractive index of the liquid must be taken into account. A greater ring, however, does necessarily correspond to smaller drops and though the ring-measurements may not give us the exact size of the drops, for comparative measurements they are none the less useful.

Measurement of the intensity of light :—

A very sensitive photo-cell was employed in these measurements and consequently, a lamp working on 230-volts D. C. supply mains could not be used on account of the fluctuations in its intensity. A 500-watt electric lamp (lamp B), working on a 120-volt independent steady battery was therefore used as the source of light. The light of this lamp was brought to a focus at a very distant point. The light after passing through the flask travelled along the axis of a metal cylinder about 33 cm. in length and 11 cm. in diameter. The inside of this cylinder was blackened. At its end facing the flask this cylinder carried a disc, having a central aperture nearly 1.5 cm in diameter. The further end of the cylinder carried a big lens of about 25 cm. focal length. With this lens the central parallel beam of light could be focussed on the slit of a monochromator, which was used to isolate different regions of the visible spectrum. The photo-cell was mounted in a wooden box having a small window through which it received the monochromatic radiation. The box of the photo-cell was coated on the outside with wax to prevent leakage. The observations were carried out in a dark room and the photo-cell box

as well as the monochromator was covered by a black cloth to cut out stray light.

The diagrammatic layout of the apparatus as seen from above is given in fig. 4.

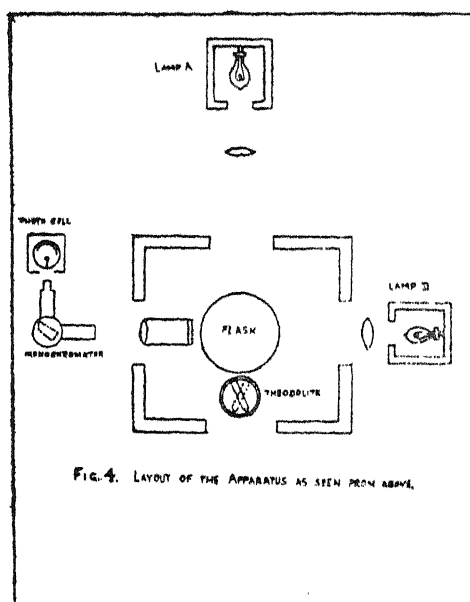


FIG. 4. LAYOUT OF THE APPARATUS AS SEEN FROM ABOVE.

The photo-electric current was amplified by means of a one-stage direct current vacuum-tube amplifier. The circuit is shown in fig. 5.

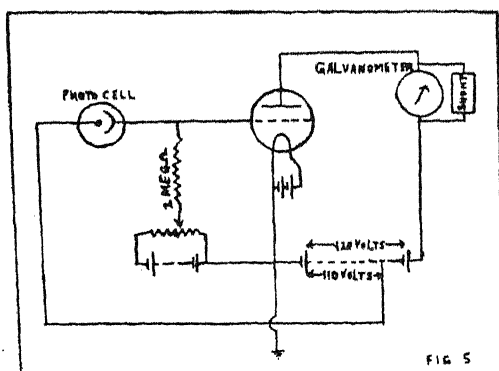


FIG. 5

The galvanometer was shunted by a resistance of about 0.2 to 0.4 ohm, so that it was rendered dead-beat and the deflection did not go beyond the scale. Lamp and scale were used to magnify the deflection. The scale was kept at a distance of about 4 metres from

the mirror of the galvanometer (this mirror was concave and a fine sharp image of a filament of the lamp could be focussed on the scale). The scale was about half a metre long and was divided into 700 parts. The measurements were taken correct to 5 divisions, so that the values of the transmission-ratio were correct to about 2%. (Note :—The ratio of the intensity of the light after passing through a cloud to its original intensity is called the transmission ratio and is given by the ratio of the deflections of the galvanometer with and without the cloud in the flask, the intensity of the beam being regarded as proportional to these deflections).

As the photo-cell was not equally sensitive to all colours, being in fact far more sensitive to the red than to the blue light, a rheostat was included in the circuit of the lamp B and the resistance was so controlled as to have almost a full scale deflection for all the wave-lengths used. The following mean wave-lengths were chosen for this investigation :—4600, 5100, 5600, 6100, and 6600 A. U.

A TYPICAL EXPERIMENT

As has already been remarked the atmospheric pressure and the room temperature were noted, before and after each set of experiments; variations of a few millimetres, in the pressure, and changes in the temperature of about half a degree at the most, were found to take place; but they were inevitable and to avoid any error on their account, in some cases a fairly large number of observations was taken and in others the measurements were made as quickly as possible, so that the whole set was completed before any appreciable change in the temperature and pressure had taken place. These variations were, however, small and their effect could be neglected.

The monochromator was then arranged so that the beam was sharply focussed on its slit. The photo-cell box was kept in its proper position and both the monochromator and the photo-cell box were then covered by a black cloth.

A trial intensity measurement was then taken in the following way :—

The grid-bias rheostat was first so adjusted that the galvanometer pointer was at one end of the scale; the lamp B (the one for intensity measurements) was then switched on to see what deflection was obtained; if the deflection was not full-scale, the shunt of the micro-ammeter was changed, the G. B.-rheostat readjusted and again the deflection noted. This process was repeated until a full-scale deflection was obtained.

Observations were always started with the wave-length 4600 A. U., for which the photo-cell was least sensitive and the lamp

required its full current to give a large deflection. Longer wave-lengths were then taken up one after another, the intensity of the lamp being regulated by the rheostat, the adjustment of the G. B.-rheostat and the shunt of the micro-ammeter remaining thus the same for all wave-lengths.

The tank was then partially evacuated and a small expansion made in the flask. Nuclei from burning incense-stick were then admitted into the flask along with the outside air. When liquids other than water were worked upon, an altogether different process of introducing the nuclei and the liquids had to be adopted. The pressure in the tank was brought down to a definite value which was indicated by the manometer attached to the tank.

The amplifier was again switched on, and the position of the pointer of the galvanometer noted. The lamp B was then switched on and off a few times to see if the readings of the pointer were reproducible. When this was found to be the case the positions of the pointer with the lamp B off and on were noted ; while the lamp was still burning the expansion was made by quickly opening and closing the tap connecting the flask and the tank. The time required for this operation can be regarded as almost the same for each expansion, the constancy being, in fact, a function of the training of the hand. The new position of the galvanometer pointer was noted, the lamp B was switched off, and the lamp A switched on. The operation of switching off the first lamp and switching on the second was done by one and the same switch, the lamps working on two independent batteries. The theodolite was rotated one way (in the way in which the pointer attached to the theodolite was carried by the rotating disc along with it), and then the other way, directing the telescope-tube of the theodolite each time to the centre of the first blue ring. The tube of the telescope carried cross-wires at its end facing the flask and the rings were observed through a fine hole in an ebonite piece, which was substituted for the eyepiece. The lamp A was switched off first and then the amplifier. The readings of the base-scale of the theodolite could then be taken at leisure. The interval between the moment of expansion and the final setting of the theodolite was hardly ten seconds (this was possible after some practice) and both the measurements (for the determination of the size of the drops and of the transmission ratio) could be regarded as almost simultaneous.

(IV).

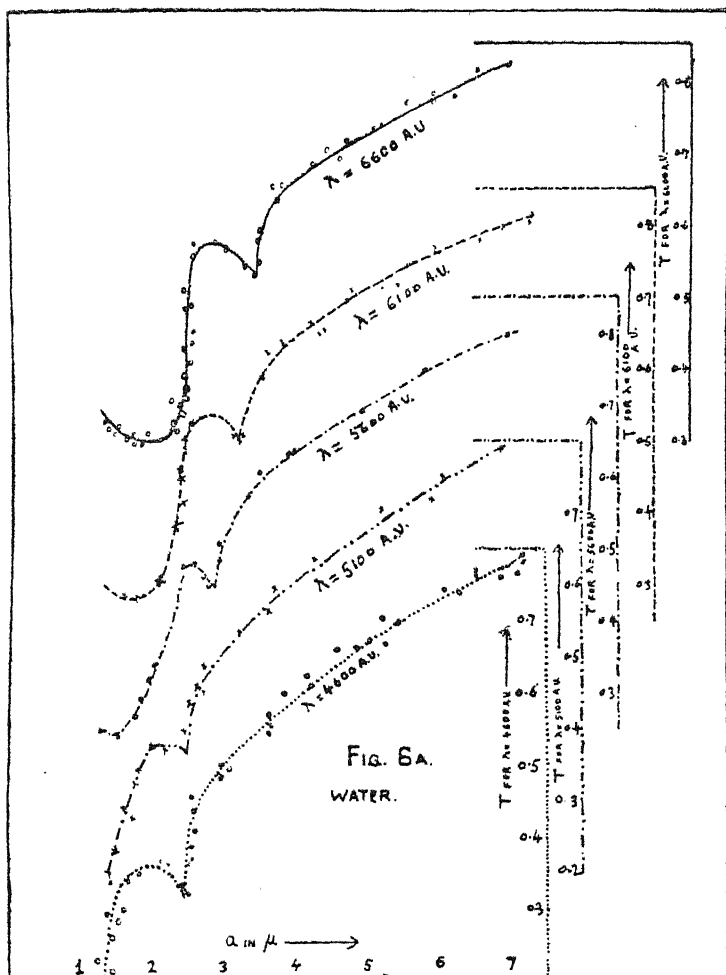
WATER.

Since data, both experimental and theoretical, are available in the case of water, this liquid has been studied in detail. Other

liquids then follow, results in each case being compared with those of water.

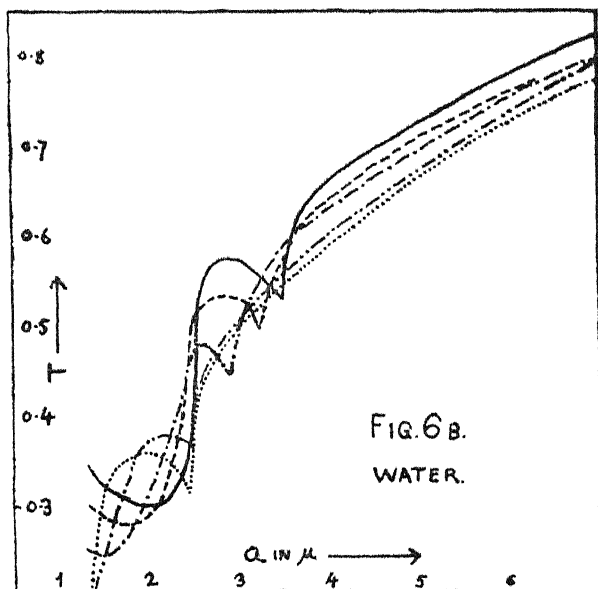
Graphs have been plotted to represent the transmission as a function of the size of the condensed drops. Graphs for water are given in fig. 6 A and B.

In fig. 6 A, the ordinate is shifted up successively and is given against each curve on the right-hand side.



It can be seen from the graphs that though the curves show the maximum and minima, these turning points do not occur at the expected values of the size of the drops. Further large drops appear to transmit red light better than blue, in contradiction with the theory (vide fig. 2). The graphs do not meet at

$a=5\mu$, as in fig. 2, but show only a slight tendency to meet even at $a=7\mu$. The curves do not show sharp turning points (excepting the first minimum). This may be attributed in the first place to the fact that the ideal curves correspond to strictly monochromatic light



whereas in the present work the beam had a dispersion of about 100 A.U. and in the second place, the clouds have been supposed to consist of uniform droplets whereas there might have been a certain number of drops having different sizes. The first minimum could have been rounded off but it is drawn sharp to show the experimentally observable difference between it and the other two turning points.

Before taking up a detailed discussion of the results obtained in the case of water, it will be useful to survey the theory and its limitations briefly.

Development and limitations of the theory :—

Whenever the phenomena resulting from an incident electromagnetic radiation are to be studied macroscopically the whole process is split up into reflection and refraction on one side and scattering on the other, and each item is studied separately. Such considerations are, therefore, made for small particles to begin with.

If the particles are very small as compared to the incident wavelength, the scattering alone need be considered, and we obtain the well-known relation due to Rayleigh. If, however, the drops are not

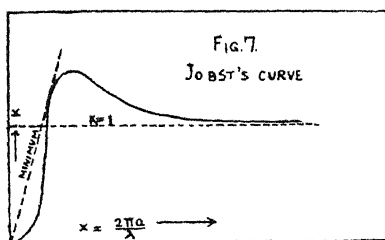
small in comparison with the wave-length, the effect due to scattering may be neglected since reflection and refraction play a prominent role in this case. Wiener¹⁶, Mecke¹⁴ and Pokrowski¹⁷ tried to solve this problem on certain assumptions, which rendered their considerations valid only in special cases; their results are not applicable when the sizes of the particles are of the same order of magnitude as the wave-length.

Mie¹¹ has carried out an exact calculation of scattering and absorption on the ground of the electro-magnetic theory of light. These calculations hold good for any size of the particle and for any value of the wave-length, the only objection to these calculations being the extension of the physical constants obtained from macroscopic investigations to the microscopic particle under consideration. The application of his formula is rendered very elaborate on account of the numerous difficulties encountered in the calculations. Consequently, investigators who undertake to verify Mie's theory restrict themselves to cases where the ratio of the size of the particle to the wave-length can be regarded as small.

If the sizes of the particles are of the same order of magnitude as the wave-length, Mie's theory can be rendered applicable in two different ways:

- (i) the calculations are simplified by using suitable tables; or
- (ii) easily calculable expressions are obtained by suitably transforming Mie's formula.

Blumer¹⁸ has followed the first method and calculated the scattering by particles 0.5μ to 1.0μ in diameter. The second method has been followed by Debye¹², Jobst¹³ and others. Jobst, in particular, succeeded in calculating the total scattered or absorbed light for any ratio of the diameter of the particle to the wave-length. Fig. 7 shows the curve obtained by Jobst.



This curve gives the relation between the scattered light and the size of the particle and the wave-length. The size of the particle remaining the same, the absorption first increases with decreasing wave-length very steeply, becomes flat very rapidly and attains a

maximum and then has a feeble slope and an asymptotic approach to the ordinate $K = 1$. From this curve it is seen that for a particular size of the particle, only one wave-length will have a minimum transmission.

Stratton and Houghton¹⁰ followed Jobst very closely but they investigated the region of small values of $x = 2\pi a/\lambda$ and obtained in addition to the maximum of Jobst's curve one more maximum, which is much flatter, and a minimum between these two maxima (vide fig. 1,). The consequence of this is that for a particular size of the particle, there would be a minimum transmission for two wave-lengths and a maximum transmission for some intermediate wave-length.

Jobst and later Stratton and Houghton have carried out their calculations only for a perfectly or very nearly perfectly conducting particle. This restriction is due to the fact that the introduction of a finite value of conductivity brings in along with it difficulties of calculations. In the absence of an accurately worked out K -curve, a prediction about the nature of scattering and absorption in a particle having finite conductivity is impossible to make.

These considerations hold only for a single particle. When a number of particles are present, as in a cloud, the effect of the neighbouring particles will have to be taken into account. There may be, for example, multiple scattering and interference taking place and it is difficult to say how these would affect the transmission.

A comparison of the results obtained in this investigation with those of other workers and with the theory may now be taken up. The experiments can give results which make it possible to have only a qualitative comparison with the theory; for the theory deals with a single perfectly conducting particle whereas results to be compared have been obtained from measurements on a collection of particles having a finite conductivity.

Comparison of experiment with the theory:—

Of all the works mentioned in the beginning those of Külb⁸ and Houghton⁷ are useful for comparison, since they have given the sizes of the particles in their clouds. It is possible to indicate what the size of the particles in the clouds of the rest of the investigators might have been, but it is of little use to do so, since there would be no verification for the same. Kobayasi & Nukiyama⁹ obtain, in the case of water, results similar to those of Houghton and we may assume (though they have not given the size of their particles) that the size of their particles was the same as that of Houghton's.

Külb has worked on artificial clouds of opaque particles such as NH_4Cl etc. His results may, therefore, be expected to show only a similarity but no agreement with the results obtained with water drops. This is found to be the case. He got a maximum transmission between $\lambda = 25000$ A.U. and $\lambda = 30000$ A.U., and a minimum transmission for $\lambda = 5500$ A.U., for all the clouds he investigated. He tries to explain his results with the help of Jobst's curve (fig. 7). The minimum in his results could be explained by this curve but not the maximum. He was, however, able to show that Blumer's¹⁸ results indicated the existence of more than one turning points in the transmission-wavelength curves and that his result was, therefore, not surprising. The maximum in the infra-red was, according to him, due to some unknown causes, quite distinct from those responsible for the minimum in the visible region. Houghton's curve (fig. 1), however, not only explains Külb's maximum but also predicts a minimum in farther infra-red. Külb has not gone beyond $\lambda = 42000$ A.U. and this prediction cannot, therefore, be verified at present.

Kobayasi & Nukiyama⁹ obtained in the case of NH_4Cl clouds a sharp maximum transmission at $\lambda = 4580$ A.U. in contrast to Külb's minimum at $\lambda = 5500$ A.U. and maximum at $\lambda = 26000$ A.U. This disagreement might be due either to an extraordinary difference in the particle-size in the two cases or to the non-uniformity of the particles employed by Kobayasi & Nukiyama. Houghton's curve cannot explain both the maxima since it admits the existence of only one maximum.

In the case of water they get two maxima of transmission, a weak one for $\lambda = 3600$ A.U. and a sharp one for $\lambda = 4780$ A.U. This shows that the clouds of water in their experiments must have contained quite an appreciable percentage of drops having a size smaller than that responsible for the second (sharp) maximum. Similarly in the case of smokes from incense etc. they obtain two maxima which must also be due to the same cause.

Houghton⁷ obtained a maximum transmission for $\lambda = 4900$ A.U. The drops in his clouds were 2 to 3 microns in diameter. He has calculated the size of the drops for which there would be a maximum transmission at 4900 A.U. according to his curve. He gets for the diameter of the drops a value of 1.7μ . Thus the ratio of the observed to the calculated value of the size of the drops comes out to be about 1.2 to 1.8. The observed values have, therefore, a considerably greater magnitude than that given by the theory.

Instead of varying the wave-length and keeping the size of the

drops the same, in the present investigation, the wave-length was kept constant for one curve and the size of the drops was varied.

The verification can be effected as follows:—

(1) Verification of equation (1a),

(2) " " " (2a),

& (3) " " the absolute magnitudes of the drops at which the maximum and the minima of the a-T curves occur for different wave-lengths.

(1) & (2) are represented by tables 2-3 below. These have been obtained from table 1, which gives the values of $n a_m$ (vide fig. 6A) ($n a_m$ denotes the radius of the drops at which occurs the m th turning point of the a-T curve corresponding to the wave-length λ_n).

TABLE 1.

| | | Min. 1. | Max. | Min. 2 |
|-----|-------------------------|---------|---------|---------|
| n | λ_n in A. U. | $n a_1$ | $n a_2$ | $n a_3$ |
| 1 | 6600 | 3.5 | 2.9 | 2.0 |
| 2 | 6100 | 3.2 | 2.8 | 1.8 |
| 3 | 5600 | 2.9 | 2.6 | 1.4 |
| 4 | 5100 | 2.5 | 2.2 | ? |
| 5 | 4600 | 2.4 | 2.0 | ? |

TABLE 2

| λ in A. U. | 6600 | 6100 | 5600 | 5100 | 4600 | |
|-----------------------|-----------|------|------|------|------|-------------|
| | Observed. | | | | | Calculated. |
| $\frac{n a_2}{n a_1}$ | 0.83 | 0.87 | 0.90 | 0.88 | 0.83 | 0.86 |
| $\frac{n a_3}{n a_1}$ | 0.57 | 0.55 | 0.48 | ? | ? | 0.36 |

TABLE 3

| n | $\frac{n^{a_1}}{1^{a_1}}$ | $\frac{n^{a_2}}{1^{a_2}}$ | $\frac{n^{a_3}}{1^{a_3}}$ | $\frac{\lambda_n}{\lambda_1}$ |
|-----|---------------------------|---------------------------|---------------------------|-------------------------------|
| 2 | 0.92 | 0.96 | 0.90 | 0.93 |
| 3 | 0.83 | 0.89 | 0.70 | 0.85 |
| 4 | 0.71 | 0.76 | ? | 0.77 |
| 5 | 0.68 | 0.69 | ? | 0.70 |

It is thus clearly seen that the relations (1a) and (2a), are fairly well satisfied, with the exception of the high experimental values for $\frac{n^{a_3}}{n^{a_1}}$, (Table 2). This exception is probably due to the theoretical value for the ratio being too small on account of the considerably low value of $x = 5$ to which n^{a_3} corresponds. As will appear later there is much divergence between theory and experiment at this value of x ($= 2\pi a/\lambda$).

Table 4 gives the values of the sizes of the drops for which the turning points (in the transmission-radius curves fig. 6A,) ought to occur, according to theory.

TABLE 4

| n | λ_n | n^{a_1} | n^{a_2} | n^{a_3} |
|-----|-------------|-----------|-----------|-----------|
| 1 | 6600 | 1.47 | 1.26 | 0.52 |
| 2 | 6100 | 1.36 | 1.16 | 0.48 |
| 3 | 5600 | 1.24 | 1.07 | 0.44 |
| 4 | 5100 | 1.14 | 0.97 | 0.41 |
| 5 | 4600 | 1.02 | 0.88 | 0.37 |

A comparison of these values with those of Table 1 will show that the third part of the verification is not at all satisfied. This discrepancy between the observed and calculated values of n_m can

be suitably represented by the ratio of these values. Table 5 gives these ratios for different wave-lengths.

TABLE 5

| λ in A. U. | $\frac{o^{a1}}{c^{a1}}$ | $\frac{o^{a2}}{c^{a2}}$ | $\frac{o^{a3}}{c^{a3}}$ |
|-----------------------|-------------------------|-------------------------|-------------------------|
| 6600 | 2.34 | 2.33 | 3.85 |
| 6100 | 2.38 | 2.44 | 3.75 |
| 5600 | 2.32 | 2.42 | 3.18 |
| 5100 | 2.19 | 2.26 | ? |
| 4600 | 2.35 | 2.27 | ? |

It is seen that the values of the ratio in the second and the third columns of this table are nearly the same and fairly constant, showing a slight tendency to decrease with the wave-length. The values in the fourth column are rather too high but they show a definite and much greater tendency to decrease with the wave-length. The ratios in the first two ratio-columns are higher than 1.8, which is the maximum value of the same ratio for the particles in Houghton's clouds. As the value of the size of the drops in a cloud goes on increasing, the condition necessary for approximate calculations (viz. that the value of x should be small) goes on being more and more violated. Already when the drops are 2 to 3 microns in diameter, the ratio attains a maximum value of 1.8; it is no wonder, therefore, that a value as high as 2.4 is obtained for the same ratio with drops 2.6 to 14.4 microns in diameter.

The considerably high value (3.8-3.1) in the last column of Table 5 may partly be due to the fact pointed out by Mecke¹⁴ that small drops do not behave as opaque discs and that the determination of the size of the drops from corona rings is, therefore, uncertain when these drops are small; yet it is not possible to say how much credit may be given to this fact in raising the above values. These high values correspond to $x=5$. Had Houghton carried out his investigations in the infra-red as well, he would have, according to the theory, obtained a minimum transmission for some wave-length. It would have then been possible to determine the size of the drops from this wave-length and from this, the ratio of the

observed to the calculated value of the size of the drops. This ratio would have corresponded to $x=5$, and it would have then appeared how much the high values owe to $x=5$ and how much to Mecke's hypothesis. In the absence of the required data nothing can be said definitely. There are, however, some points which show that these high values are due to 5 being probably too low a value of x , at which the third turning points occur:—

- (1) The value 1.1 obtained for the ratio of the sizes of the drops determined by the corona ring method and from the law of Stokes was found to be practically the same for all the sizes of the drops (1 to 8 μ in radius).
- (2) There is practically complete agreement between theory and results, so far as verification (2) is concerned (vide Table 3,). This verification is independent of the values of x .
- (3) The ideal curves for transmission (fig. 2,) do not show agreement with Rayleigh's theory when the size of the drops is small in comparison with wave-length (i.e. when x is small).

In order to verify Mie's theory, investigators generally restrict themselves to particles small in comparison with the wave-length. Blumer tried to extend the work to particles 0.5 to 1.0 microns in diameter. Külb carried out the extension to particles 1.2 to 2.1 microns in diameter; Houghton's particles were 2 to 3 microns in diameter; and the particles in the present work ranged between 2.6 and 14.4 μ in diameter. Külb found that though his curves could be explained with the help of some of Blumer's calculations, in general there was no agreement between his results and Blumer's. Similarly though Houghton's results agree in a general way with those of the present work there is an appreciable difference in details. It is, therefore, difficult to decide whether this disagreement between the theory and the experiment is due to the incompleteness either of the theory or of the calculations or due to the extension of physical constants obtained from macroscopic observations to microscopic particles or due to all these put together.

In conclusion it may be remarked that one can only try under the present circumstances, to indicate a possible connection between theory and experiment. An extension of the theory and its verification by experiment is only too desirable and perhaps only then will the points be cleared up that to-day seem to be obscured by want of definite knowledge about the processes that occur when an electromagnetic radiation is incident on a multitude of non-conducting

particles having size much greater than that of the incident wavelength.

(V.)

OTHER LIQUIDS.

Other liquids are now taken up one by one and each is dealt with separately and compared with water.

The following typical liquids have been chosen :—

| | Relative density. | Refractive index. |
|-------------------------|-------------------|-------------------|
| 1. Chloroform | 1.50 | 1.45 |
| 2. Carbon Tetrachloride | 1.59 | 1.46 |
| 3. Kerosene | 0.82 | 1.45 |
| 4. Alcohol (Ethyl) | 0.79 | 1.36 |
| 5. Toluene | 0.87 | 1.50 |
| 6. Aniline | 1.02 | 1.59 |

PRELIMINARY ARRANGEMENTS.

Introduction of liquids into the flask :

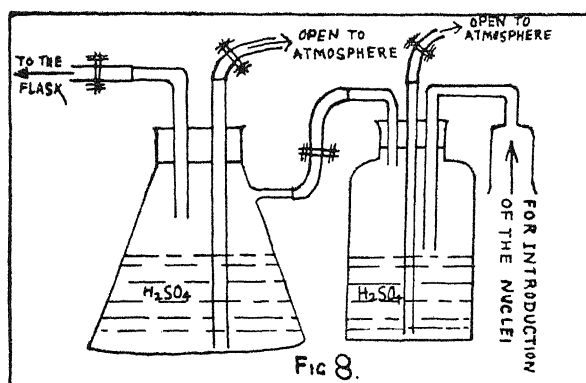
When liquids other than water are to be used in the flask, a precaution is necessary. Not only must the air that is admitted to the flask after each expansion (to bring the pressure upto that of the atmosphere) be free from water vapour but also the flask should not contain any water vapour before the introduction of the liquid. The quantity of water vapour ordinarily present in the air is quite sufficient to vitiate the results. In the first place, the cloud becomes heterogeneous and most unsteady ; and in the second, most of the drops are composed of water.

In order, therefore, that there should not be any initial quantity of water vapour in the flask at the time of the introduction of the liquid, the air inside the flask was pumped out several times and its place was filled with outside air after passing it through strong sulphuric acid. When the flask was thus practically completely freed from water vapour, which fact could be ascertained from the absence of condensation even for a very large value of the expansion, the liquid was introduced into the flask by a tube (not shown in fig. 4) passing through the cork, the principle of syphon being employed. This arrangement is also useful in adding fresh quantities of liquids without removing the cork, if the liquids are volatile.

Introduction of the nuclei, keeping out water vapour :

In order to ensure that no water vapour entered the flask when the nuclei obtained by burning incense stick were introduced, the following arrangement was adopted :—

The nuclei were first introduced in a small bottle containing strong sulphuric acid; here they were allowed to remain for some time. Air was then drawn into the bottle through the acid and the nuclei were thus carried into the flask by a current of dry air. The communication between the bottle and the flask was made through an additional vessel containing strong sulphuric acid. Dry air free from nuclei could also be thus admitted to the expansion chamber whenever required. The diagram of the arrangement is given in fig. 8.



Note:—For each liquid, the magnitude of expansion was determined by trial, so that the quantity of the liquid condensed was neither too great nor too small. This was done by obtaining the transmission ratios for different densities of clouds.

CHLOROFORM.

Fig. 9 gives the transmission-curves for Chloroform.

The curves are similar to those for water in all respects.

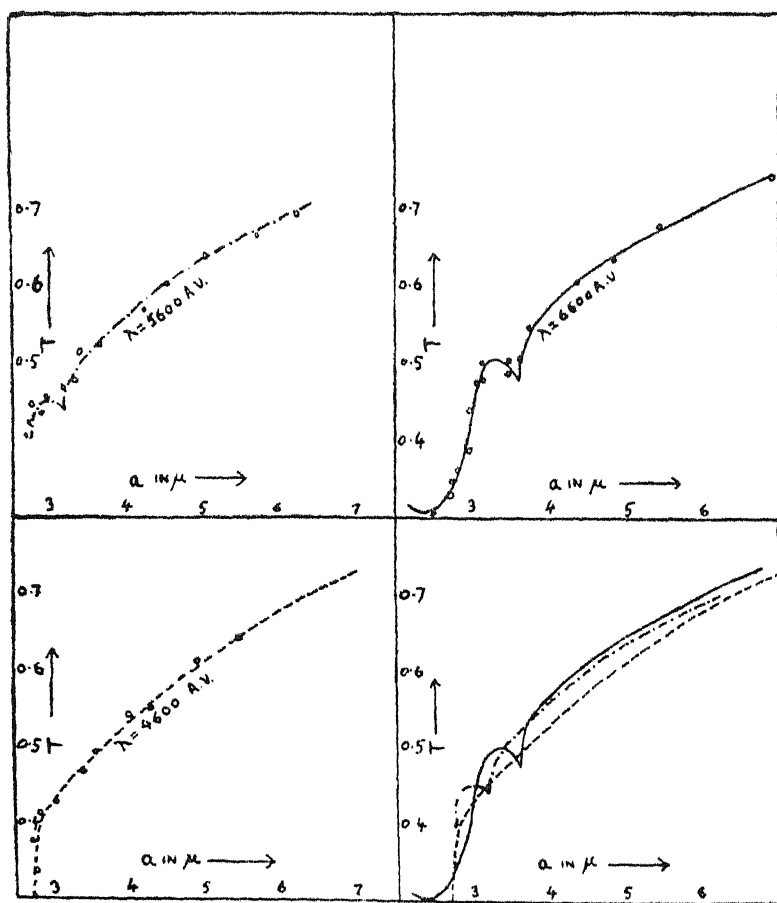


FIG. 9. CHLOROFORM.

Table 6 gives the values of n_{am} .

Tables 7-8 represent verifications (1) & (2) respectively.

TABLE 6

| n | λ_n | n^{a_1} | n^{a_2} | n^{a_3} |
|-----|-------------|-----------|-----------|-----------|
| 1 | 6600 | 3.60 | 3.30 | 2.30 |
| 2 | 5600 | 3.20 | 2.90 | ? |
| 3 | 4600 | 2.70 | ? | ? |

TABLE 7

| λ | 6600 | 5600 | Experimental values for water :— |
|---------------------------|------|------|-------------------------------------|
| $\frac{n^{a_2}}{n^{a_1}}$ | 0.91 | 0.90 | |
| $\frac{n^{a_3}}{n^{a_1}}$ | 0.64 | ? | |
| | | | 0.86 |
| | | | 0.53 |

TABLE 8

| n | $\frac{n^{a_1}}{1a_1}$ | $\frac{n^{a_2}}{1a_2}$ | $\frac{\lambda_n}{\lambda_1}$ |
|-----|------------------------|------------------------|-------------------------------|
| 2 | 0.89 | 0.88 | 0.85 |
| 3 | 0.75 | ? | 0.70 |

The results are thus in agreement with the theory.

CARBON TETRACHLORIDE

Fig. 10 gives the transmission curves for CCl_4 .

The curves are similar to those for water in all respects.

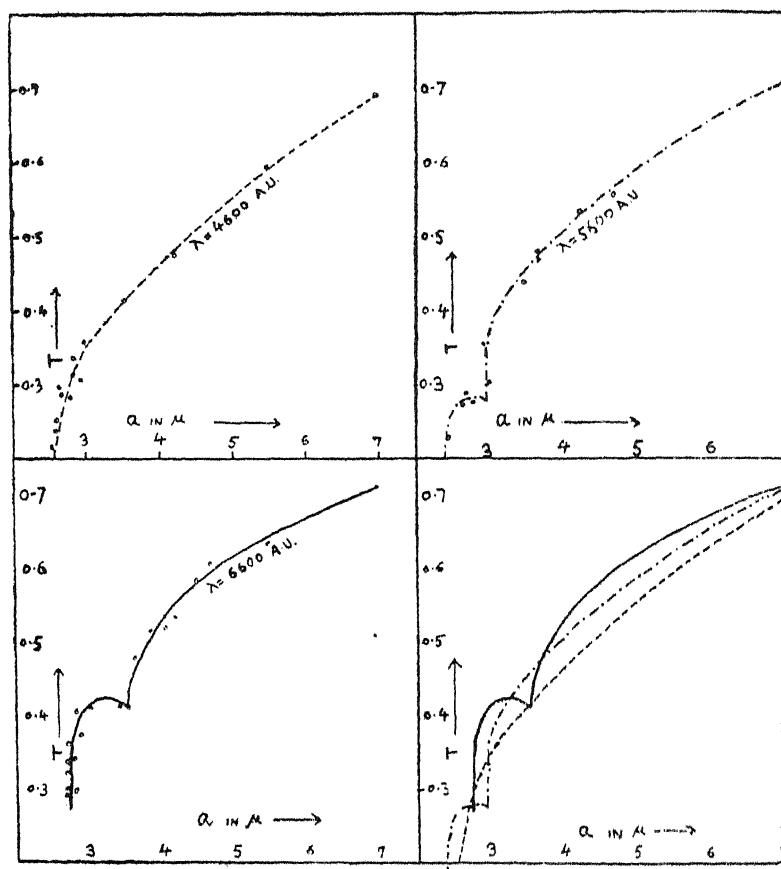


FIG.10. CARBON TETRACHLORIDE.

Table 9 gives the values of n_m .

Tables 10-11 represent verifications (1) & (2) respectively.

TABLE 9

| n | λn | n^2_1 | n^2_2 |
|-----|-------------|---------|---------|
| 1 | 6600 | 3.50 | 3.25 |
| 2 | 5600 | 2.95 | 2.8 |
| 3 | 4600 | 2.50 | ? |

TABLE 10

| λ | 6600 | 5600 |
|-----------------------|------|------|
| $\frac{n^2_2}{n^2_1}$ | 0.93 | 0.95 |

Experimental value
for water :—

0.86

TABLE 11

| n | $\frac{n^2_1}{1^2_1}$ | $\frac{n^2_2}{1^2_2}$ | $\frac{\lambda n}{\lambda_1}$ |
|-----|-----------------------|-----------------------|-------------------------------|
| 2 | 0.84 | 0.86 | 0.85 |
| 3 | 0.71 | ? | 0.70 |

The results are thus in agreement with the theory.

KEROSENE.

Fig. 11 gives the transmission-curves for Kerosene.

The curves are similar to those for water in all respects.

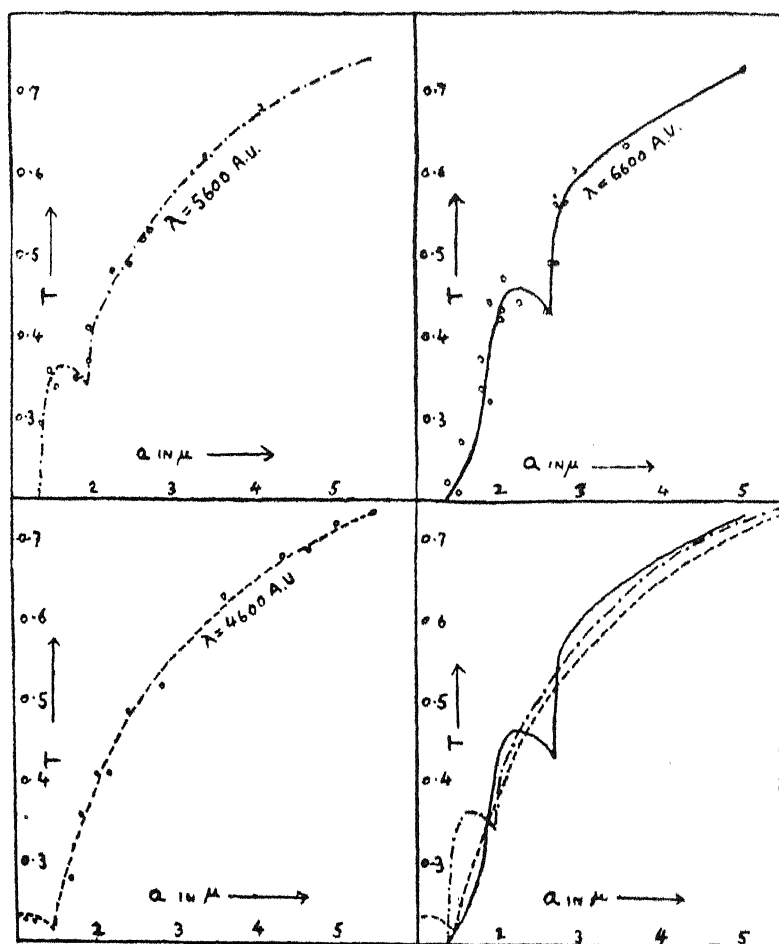


FIG. 11. KEROSENE.

Table 12 gives the values of n_{am} .

Tables 13-14 represent verifications (1) and (2) respectively

TABLE 12

| n | λn | n^{a_1} | n^{a_2} |
|-----|-------------|-----------|-----------|
| 1 | 6600 | 2.70 | 2.30 |
| 2 | 5600 | 1.95 | 1.65 |
| 3 | 4600 | 1.45 | 1.10 (?) |

TABLE 13

| λ | 6600 | 5600 | 4600 |
|---------------------------|------|------|----------|
| $\frac{n^{a_2}}{n^{a_1}}$ | 0.85 | 0.85 | 0.76 (?) |

Exp. value
for water:

0.86

TABLE 14

| n | $\frac{n^{a_1}}{1^{a_1}}$ | $\frac{n^{a_2}}{1^{a_2}}$ | $\frac{\lambda n}{\lambda_1}$ |
|-----|---------------------------|---------------------------|-------------------------------|
| 2 | 0.72 | 0.72 | 0.85 |
| 3 | 0.54 | 0.48 | 0.70 |

The results do not satisfy verification (2) ; kerosene thus forms a partial exception to the theory. It is, however, to be noted that the experimental values show a remarkable agreement among themselves.

ALCOHOL.

Fig. 12 gives the transmission-curves for Alcohol.

This liquid is an exception to the general theory, the curves for different wave-lengths being practically identical.

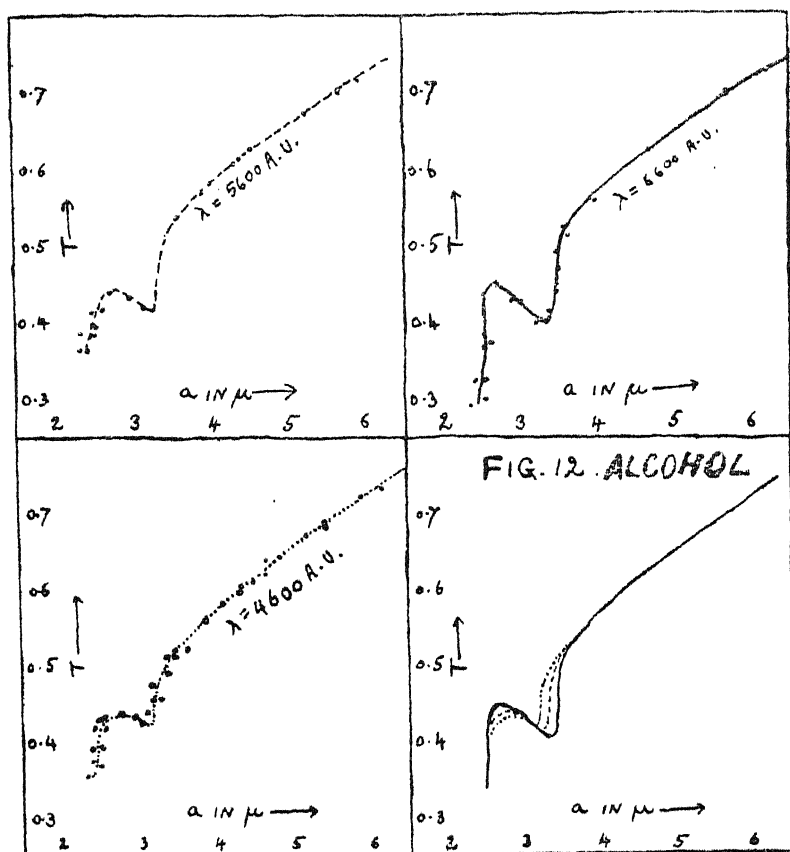


Table 15 gives the values of $n_a m$.

TABLE 15

| n | λn | n^a_1 | n^a_2 |
|-----|-------------|---------|---------|
| 1 | 6600 | 3.30 | 2.70 |
| 2 | 5600 | 3.15 | 2.80 |
| 3 | 4600 | 3.10 | 2.85 |

n^a_1 appears to increase very slightly with the wave-length while n^a_2 shows an opposite tendency.

TOLUENE.

Fig. 13 gives the transmission-curves for Toluene.

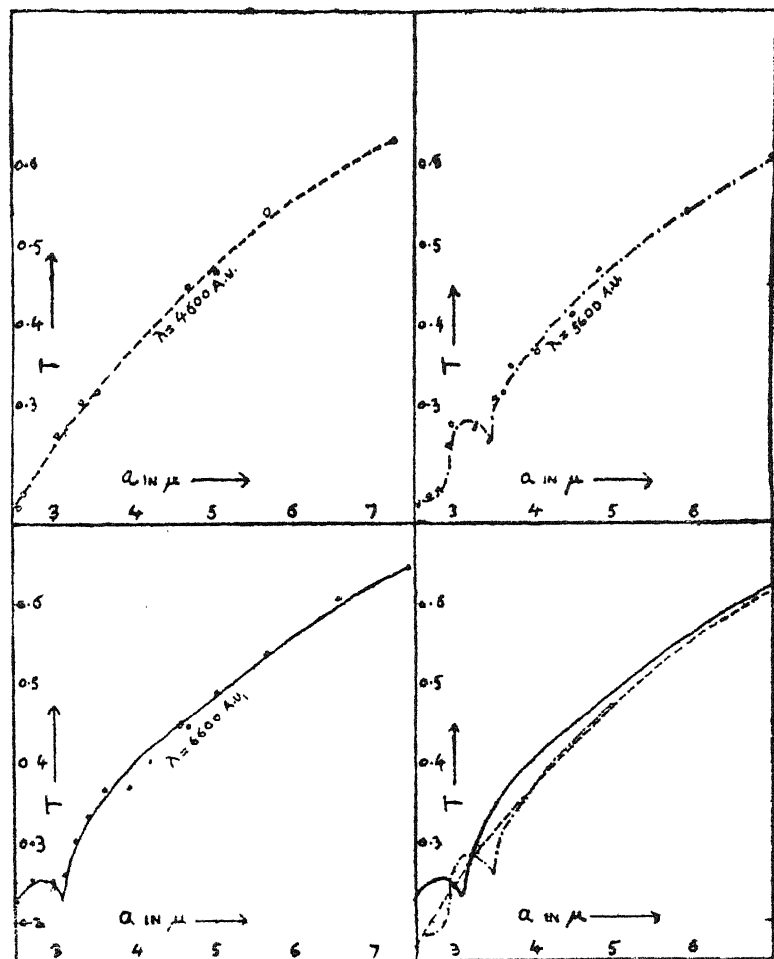


FIG. 13. TOLUENE.

This liquid is another exception to the general rule, the values of n_{am} increasing with decreasing wave-length, as table 16 clearly shows.

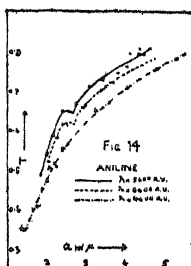
TABLE 16

| n | λn | n^a_1 | n^a_2 |
|-----|-------------|---------|---------|
| 1 | 6600 | 3.10 | 2.90 |
| 2 | 5600 | 3.50 | 3.20 |

Large drops appear to transmit red light better than blue just as in the case of water.

ANILINE.

Fig. 14 gives the transmission-curves for Aniline.



Aniline is the third exception and stands out from other liquids on account of the absorption of light occurring in it. The curves are altogether different from those for the rest of the liquids. They show that blue light is more absorbed than the red while some intermediate colour is the least absorbed. The curves for $\lambda = 6600$ and 5600 A.U. show slight turning points (it is, however, uncertain whether any turning points exist here) while there is no trace of them in the curve for $\lambda = 4600$ A.U. There is one more point of interest in these curves; whereas in other liquids which are transparent the curves tend to approach one another for large values of a , no such tendency is exhibited here. This is perhaps on account of the absorption of the light by the drops. On the other hand the curves definitely show a tendency to meet when the drops are small, indicating that the absorption has become less.

GENERAL REMARKS.

The results in the case of CHCl_3 , CCl_4 , and Kerosene are very similar to those for water. These liquids have about the same refractive index, but their densities differ. A glance at Tables 6, 9, 12 for these liquids will show that the values of n^a_m for CCl_4 are only slightly smaller than those for CHCl_3 , while those for Kerosene are much smaller. This may be due to the small density of Kerosene.

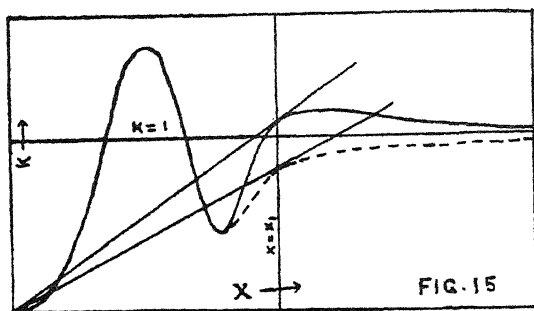
The curves for different wave-lengths are closer together and meet at a smaller value of a in the case of lighter liquids (cf. figs. 9-13).

No definite conclusions can be drawn about the effect of refractive index on the transmission.

Chloroform and Carbon Tetrachloride appear to be in agreement with the theory; Kerosene forms a partial exception; while Alcohol, Toluene, and Aniline show no agreement whatever. This is not surprising. Taking into consideration the limitations of the theory it would appear that agreement with the theory should really form the exception.

On the nature of the K-curve.

It was found in the case of water that red light was transmitted better than blue by large drops. This is at variance with the theory. With the exception of alcohol and aniline, in all other liquids investigated here the same result was obtained, viz., that red light was transmitted better than blue by large drops. It thus appears that the K-curves for these liquids should have similar nature for large values of x and that they should tend asymptotically to $K=1-0$ i.e. from below, as indicated by the broken line in fig. 15 and not to $K=1+0$ i.e. from above, as shown by the full line. The figure shows how this asymptotic approach from below can be in conformity with the other results obtained from the theory: The points of contact of the tangents from the origin to the two curves (broken and full) have the same abscissa.



SUMMARY.

The present work was undertaken to verify Stratton and Houghton's theory of the transmission of light through clouds of water.

The paper gives a method of analysis for the verification of the above theory and describes suitable experimental arrangements for obtaining the necessary data.

The results obtained with water are discussed in detail and are found to agree tolerably well with the theory, with all its limitations.

In order to obtain information about the influence of the refractive index on the transmission, six other typical liquids were also investigated. Transmission curves for different wave-lengths were found closer together in the case of lighter liquids but no definite conclusions could be arrived at as regards the effect of the refractive index.

Two of these liquids showed good agreement with the theory; one liquid showed only a partial agreement; and the remaining three exhibited no agreement whatever.

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IRON ARC SPECTRUM IN THE INFRA-RED.

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Until some years ago, few serious attempts were made to investigate the region of the spectrum beyond $0.8\ \mu$. Photographic plates sensitive to region upto about $11500\ \text{\AA}$. have been made available on a commercial scale only very recently, and this has facilitated much of the spectroscopic work in this region. However one great disadvantage under which such work suffers in this country, is the rapid deterioration of the infra-red plates due to high temperature, unless special care is taken to store the material in a constant temperature cold chamber.

The present work arose as a result of infra-red equipment that has been made specially available to us very recently. With a view to obtain further knowledge of some of the diatomic molecules, in this less investigated region, we undertook some preliminary investigations on the technique, such as the photography and the wavelength standards. For all spectroscopic work in the visible as well as in the ultraviolet, the International Astronomical Union has fixed iron wavelength standards. No such standards have been officially adopted yet for the infra-red, though for practical purposes, the mapping of spectra in this region is mostly done by referring to argon and neon or the solar and atmospheric lines where available. The International Astronomical Union in their Report¹ of 1928, have suggested further measurement of the iron arc lines especially in the region $\lambda\ 8327$ and $\lambda\ 8824$. In the summary of the recommendations made, further search for suitable lines as standard in the infra-red has been advocated.

Considerable data has accumulated since the publication of the I. A. U.'s Report¹. Important among these are the results of Babcock², Meggers and Kiess³, Dingle⁴ and recently of Meggers⁵. Kayser and Konen⁶ have compiled a list of iron lines observed by different authors. Except the very recent work of Meggers,⁵ which is considered to be thorough and exhaustive, the data cannot be said to be conclusive unless large confirmatory material is available. It is also known that the sensitivity of the photographic emulsions varies with different makes and is generally supposed to fall with time

after sensitizing with ammonia. On account of this, the results of different authors may not agree with regard to the numerousness of lines, though the accuracy of readings can be guaranteed according to instruments used. The object of this paper is not so much to improve upon the accuracy as to give a catalogue of lines recorded on our plates in comparison to data already existing.

EXPERIMENTAL.

The iron arc was run on 230 volts at a current of 3 amps in air at 1 atmosphere. The rods used were of commercial type. The spectrum was photographed on the Hilger E_{305} spectrograph available for a range from 4000 Å. to 15000 Å. The dispersion on this, for higher wavelengths was considerably smaller than for the visible region. The spectrum from 8000 Å. to 9000 Å. covered about 8.2 mms on the plate and that from 9000 to 10000 Å. about 7 mms. The plates used were the Kodak III-Q and III-L types. The mercury arc spectrum photographed on the former could give the 11287 line with ease even without further sensitizing. In order to reduce the time of exposure, we tried at first to photograph the infra-red region without filtering out visible radiations, but on experience it was found out that for the sake of fineness of lines, facility of measurement and accuracy of results in this low dispersion region, absolute clearness of background was necessary. This could not be attained unless the strong visible radiations, which cause general fogging are entirely cut out. The III-L type plate was very sensitive to region from 7000 Å. to 9000 Å. after sensitising with ammonia and with filter a few seconds being necessary to bring out this region on the plate. The advantage that we could gain in this short exposure was the reduction of slit-width to dimension consistent with the fineness of lines in the spectrum. These results are illustrated in plates I and II.

For spectrum beyond 9000 Å., the III-Q type plate was found much better after sensitizing. But these plates were found to deteriorate very quickly and even with cold chamber storage they showed a tendency to develop marks characteristic of old plates, though their life is somewhat increased by such storage.

No external comparison spectrum was taken to map the spectrum, but in any portion chosen for measurement, three suitable internal wavelengths of prominent iron lines were selected, and the intermediate wavelengths were then interpolated in the usual way. These prominent lines were selected from wavelength chart of Hilgers and from a recent paper of Zaki Uddin⁷ giving compilation of revised prominent lines. Hilger's L_1 Comparator was used for the purpose of measuring the plates.

RESULTS.

A catalogue of lines measured in the above manner is given in the table below. The first column gives our own measurements. For comparison, the corresponding values from Hilger's chart based upon Babcock², Querbach⁸, Meggers and Kiess³ are entered in column 2, and those of Dingle in column 3. It was unfortunate that we could not get to hand the paper of Meggers⁵ on the interferometric measurements for the purposes of comparison. The results of Dingle,⁴ being the measurements on 10 ft. grating, are supposed to be accurate and they contain a few more lines than those recorded in column 1 or 2.

Table giving the iron lines measured and comparative values.

| AUTHORS | HILGER'S CHART. | DINGLE. |
|---------------------------|-----------------|---------|
| 7937.18 (8) | 7937.182 | |
| 7945.97 (6) | 7945.889 | |
| 7998.95 (8) | 7998.988 | |
| 8028.95 (2) | 8028.352 | |
| 8046.40 (8) | 8046.083 | |
| 8085.10 (6) | 8085.219 | |
| 8148.80 (0) | 8149.590 M. K. | |
| 8199.45 (1) | 8198.980 | |
| 8207.60 (0) | 8207.792 | |
| 8220.60 (8) | 8220.422 | |
| 8232.20 (0) | 8232.371 | |
| 8247.50 (?) | 8248.190 | |
| 8293.70 (0) | 8293.559 | |
| 8326.95 (10) | 8327.080 | |
| 8339.70 ($\frac{1}{2}$) | 8339.447 | |
| 8365.60 (4) d | 8365.667 | |
| 8387.60 (10) b | 8387.785 | |
| 8424.30 (0) | 8424.140 M. K. | |
| 8439.65 (2) | 8439.607 | |
| 8468.40 (8) | 8468.427 | |
| 8497.60 (2) | 8497.020 | |
| 8514.10 (8) | 8514.086 | |
| 8526.90 (0) | 8526.685 | |
| 8542.10 (4) Fe? | | |
| 8582.40 (3) | 8582.299 | |
| 8611.60 (6) | 8611.837 | |
| 8621.40 (0) | 8621.550 M. K. | |
| 8661.70 (10) | 8661.920 | |
| 8674.55 (4) | 8674.772 | |
| 8688.60 (10) | 8688.640 | |
| 8710.00 (?) | 8710.280 M. K. | |
| 8757.30 (4) | 8757.160 | |
| 8763.90 (3) | 8764.02 | |
| 8793.50 (4) | 8793.380 | |
| 8824.05 (10) | 8824.180 | |
| 8838.66 (3) | 8838.36 | 8838.46 |
| 8866.80 (8) | 8866.92 | 8867.00 |
| 8919.60 (0) | 8919.95 | 8920.10 |

| AUTHORS | HILGER'S CHART. | DINGLE. |
|---------------------------------|-------------------|-------------------|
| 8944.90 (2) | 8945.15 | 8945.21 |
| 8975.40 (2) | 8975.36 | 8975.43 |
| 8999.60 (8) | 8999.54 | 8999.56 |
| 9012.30 ($\frac{1}{2}$) | 9012.10 | 9010.64 & 9012.17 |
| 9025.30 ($\frac{1}{2}$) | 9024.47 | 9024.49 |
| 9063.10 (r) | 9062.29 M. K. | |
| 9089.65 (6) | 9089.40 | 9089.43 |
| 9118.90 (2) | 9118.87 | 9118.92 |
| 9147.60 (0) d | 9147.91 | 9148.08 |
| 9210.80 ($\frac{1}{2}$) d. b. | 9209.99 M. K. | 9210.05 |
| 9258.20 (1) | 9258.4 & 9259.05 | 9258.38 |
| 9316.80 (0) ? | 9318.09 M. K. | 9318.25 |
| 9351.00 ($\frac{1}{2}$) | 9350.52 | 9350.50 |
| 9360.90 ($\frac{1}{2}$) | 9359.37 & 9362.36 | 9359.40 & 9362.40 |
| 9372.50 ($\frac{1}{2}$) d | 9372.84 | 9372.92 |
| 9401.40 ($\frac{1}{2}$) d | 9401.09 | 9401.18 |
| 9413.90 (1) | 9414.14 | 9414.13 |
| 9442.60 ($\frac{1}{2}$) v. d | 9443.98 | 9443.98 |
| 9453.30 (1) | 9454.24 | 9452.56 & 9454.35 |
| 9512.60 (1) | 9513.21 | 9513.26 |
| 9529.10 ($\frac{1}{2}$) | 9529.31 | 9529.27 |
| 9569.60 (3) | 9569.95 | 9570.02 |
| 9603.40 ($\frac{1}{2}$) b ? | | |
| 9628.00 (4) b., vd | 9626.60 | 9626.60 |
| 9654.50 (4) | 9653.18 | 9653.20 & 9657.32 |
| 9698.90 ($\frac{1}{2}$) | 9699.70 | 9699.70 |
| 9738.90 (10) | 9738.73 | 9738.64 |
| 9763.63 (4) | 9763.34 & 9763.91 | 9763.63 |
| 9800.90 (3) | 9800.42 | 9800.38 |
| 9862.50 (4) | 9861.83 | 9861.85 |
| 9887.80 (4) v. d. | 9889.11 | 9889.10 |
| 10064.7 (4) | 10065.09 | 10065.08 |
| 10146.2 (4) | 10145.64 | 10145.69 |
| 10216.5 (4) | 10216.42 | 10216.44 |

b=broad, d=diffuse, v. d.=very diffuse M. K.=Meggers & Kiess.

It can be seen from the above table that many of the intense lines agree fairly well with those of the other authors. But on account of small dispersion of spectrograph used they cannot be said to be accurate to less than tenth of an Angstrom unit. In the case of very weak or diffuse lines, the error can be as high as one Angstrom unit or more. Except for some unresolved lines, the number noted is almost the same. Errors due to non-resolution or diffuseness are to be noticed in the lines especially 9360.9, 9453.3, 9654.5, 9442.60, 9628.00 and 9887.8 in the list. The line 8542.1 which appears with appreciable intensity in our photograph has not been found in Kayser & Konen's⁶ or H. Kayser's⁹ compiled lists as due to iron. We can neither identify it with any probable impurity in the sample of iron used. It may be noted that the line at 9063.10

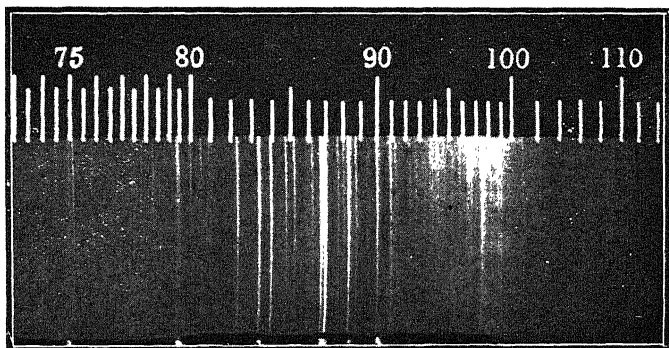


PLATE I.

Transaction 5: Iron Arc Spectrum in the Infra-red by Messrs. N. R. Tawde and V. S. Patankar.

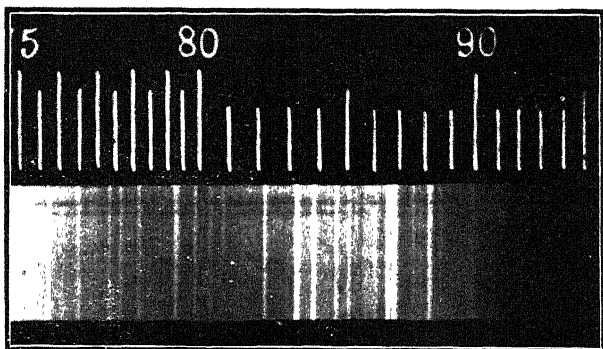


PLATE II.

Transaction 5: Iron Arc Spectrum in the Infra-red by Messrs. N. R. Tawde and V. S. Patankar.

which has been recorded on our photographs, can be identified in the list of Meggers and Kiess³, but cannot be confirmed from Dingle's⁴ recent results.

Summary: Infra-red spectrum of iron arc in air has been photographed on Hilger E 305 glass prism spectrograph and about 66 lines have been measured in the region from 7937 Å. to 10216 Å. The values have been compared to those of earlier investigators.

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- (2) Babcock, Astro. Jour. Vol. 66, p. 256, 1927.
- (3) Meggers & Kiess, Bur. Stan. Jour. Res. Vol. 9, p. 309.
- (4) Dingle, M. N. Roy. Astron. Soc. Vol. 94, p. 866, 1934.
- (5) Meggers, Bur. Stand. Jour. Res. 14, 33-40, 1935.
- (6) Kayser & Konen, Handbuch der Spectroscopie, Bd. VII.
- (7) Zaki Uddin, Current Science, 12, 620, 1935.
- (8) Querbach, Zeit. f. Physik., 60, 109, 1930.
- (9) H. Kayser. Taballe d. Haupt. d. Linienspektra. 1926.

THE TRACKS OF SWIFT NUCLEI IN PHOTOGRAPHIC EMULSIONS

By

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The following is a brief account of an investigation commenced recently in the Cavendish Laboratory, Cambridge, and now being continued in Wilson College, Bombay.

A number of methods have been devised during the past few years for recording fast nuclei. In particular, the Geiger Counter and the Wilson Expansion Chamber have been developed to an astonishing degree of perfection and the latter in particular has become an important tool of research. The method to be discussed provides yet another way of recording the tracks of swift nuclei, which has shown itself to have certain important applications. [Taylor: *Roy. Soc. Proc. A*, Vol. 150, p. 382, June 1st, 1935.]

It has been known for about 25 years that an α -particle, in its passage through the emulsion of a photographic plate, causes the silver bromide grains which it encounters to become developable. After development, the track of each particle is therefore marked out by a row of developed silver grains, and if these are sufficiently small and numerous they define the track of the particle with fair precision. As the range of the particles in the emulsion is less than one thousandth of that in air, the tracks can only be seen under a high magnification.

Ordinary commercial emulsions are not very suitable, though with special treatment of the plates good results have been obtained in certain cases by Frl. Blau and her co-workers in Vienna. For the present experiments, however, new emulsions have been devised (by the kind co-operation of the Ilford photographic company), and these are specially suitable for the recording of particles. The accompanying photographs give an idea of the kind of results which are obtained.

α -particles

Various methods have been used for the recording of α -particles. The plate may simply be soaked in a radioactive solution and then dried. The radioactive atoms are then actually in the gelatine, and

tracks are obtained distributed at random all over the plate. The number of tracks obtained depends, of course, on the time during which the plates are allowed to stand before development. Occasionally the radioactive solute forms minute crystals in the gelatine, which act as centres from which numerous α -particles are emitted. Thus one obtains a 'star' of tracks radiating from a centre, of which an example is reproduced in Fig. 1. In this case the plate had been soaked in a very weak solution of Th. (B + C).

For studying the individual tracks, it is more convenient to allow the particles to fall very obliquely on the surface of the emulsion, from a small source a few centimetres away from the plate. The experiment is done in a vacuum, so that the α -particles may reach the plate with their full energy. In this way one obtains well defined separate tracks.

It is found also that the glass of the photographic plates contains minute inclusions of radioactive substances. If these are near the surface, the particles emitted may pass out of the glass into the emulsion. An interesting example of this is shown in Fig. 2, where four tracks are seen to radiate from a point. At this point there has been a small radioactive inclusion, and the distance from this centre to the initial point of each track represents the distance which the α -particle has traversed in the glass, before rising into the emulsion.

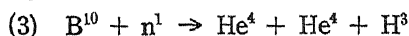
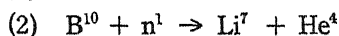
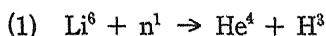
Recoil protons

When neutrons pass through the emulsion they leave no track of their own. Occasionally, however, they will come into collision with a Hydrogen nucleus, and the latter is knocked forward as a fast proton. Plates which have been exposed for some time to neutrons are found to show many such proton tracks, of maximum length corresponding to the energy of the neutrons employed. In the present experiments the maximum length found was nearly half a millimetre, corresponding to a range of some 60 cm. in air. Frl. Blau, who has investigated these protons for some time, has found even longer tracks. Fig. 3 shows a photograph of a recoil proton track in one of her plates, which she kindly sent for comparison. It will be seen that for these long tracks the large-grain process emulsion has advantages, in that the track is very clear and definite. A further point of interest is that this track shows a large angle deflection, caused by the passage of the proton near to a nucleus.

Disintegration tracks

It has further been found possible to record the tracks resulting from the disintegration of nuclei under neutron bombardment.

Lithium and Boron have been the elements studied so far. A suitable chemical compound is selected, and this is soaked into the emulsion, so that the latter is impregnated with atoms of the element in question. The plate is then exposed for a suitable time to neutrons. Occasionally a neutron makes a collision with a nucleus of Boron or Lithium, when it is found to cause a disintegration according to one of the following schemes: [Taylor and Goldhaber: *Nature*, Vol. 135, p. 341, March 2, 1935. Taylor: *Phys. Soc. Proc.*, Vol. 47, p. 873, 1935.]



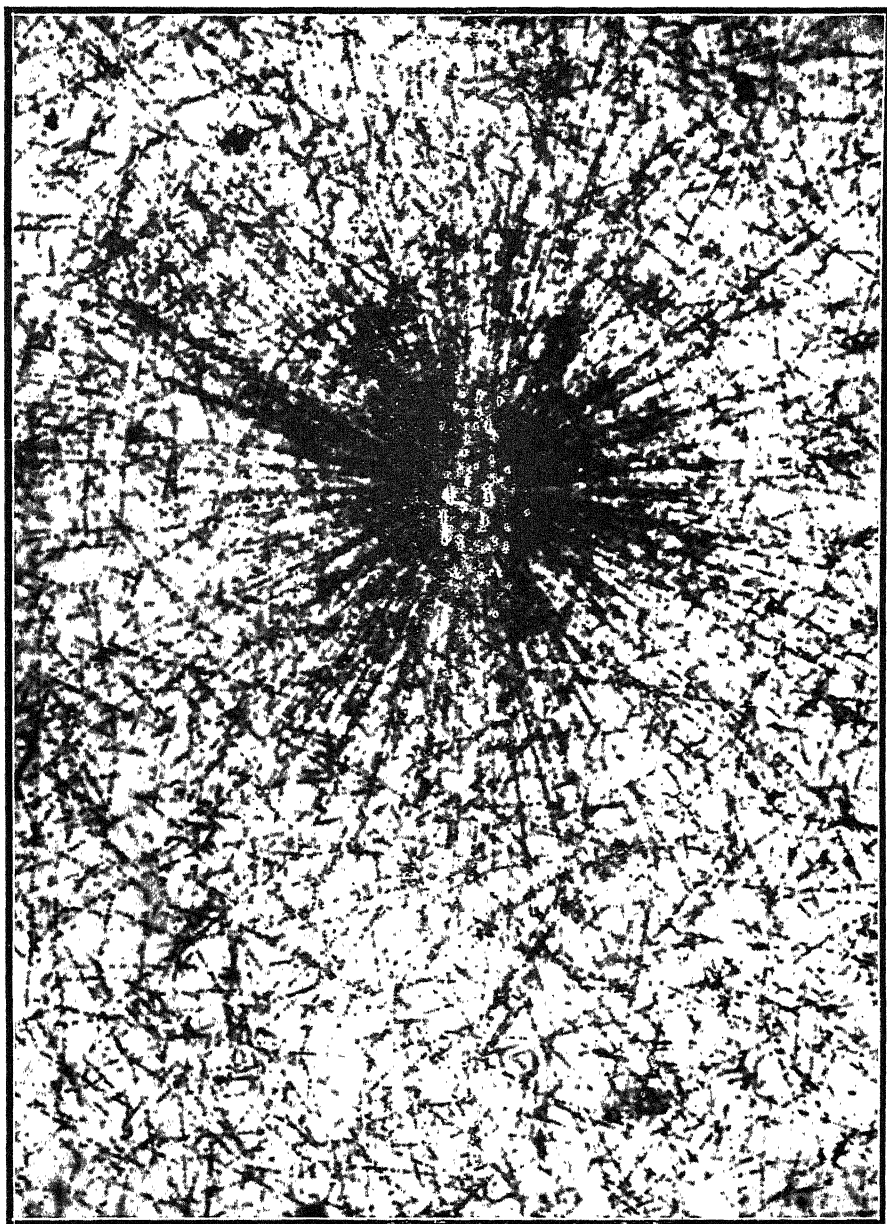
The energy appearing in the process depends upon the difference of mass between the two sides of the equation. In the case of reaction (3) the total mass of the three particles resulting from the disintegration is a little greater than the combined mass of the Boron nucleus and the neutron. Thus the reaction does not take place unless the neutron carries sufficient energy to make up for this difference of mass. Reactions (1) and (2), however, are exothermic, the sum of the masses on the right hand side of the equation being less than that on the left hand side. The difference is supplied to the resultant particles in the form of kinetic energy. Unless the bombarding neutron has large momentum, the total momentum after impact is small. Thus the two particles move away in nearly opposite directions, so that the two tracks appear as a single track.

Conclusion

The photographic method cannot be applied over such a wide field of investigation as, for example, the expansion chamber; but where applicable it has great sensitivity. In the expansion chamber the effective time of exposure is limited to a small fraction of a second, whereas the plates may be exposed to neutrons or other radiation for weeks or months. Owing to the high stopping power of the emulsion as compared with air, the equivalent volume in which tracks are obtained is many thousands of times greater than that of an ordinary chamber. Thus even extremely rare events (such as the occurrence of reaction (3)) may be recorded. These advantages make the method a powerful one, and it is now being applied to a variety of problems.

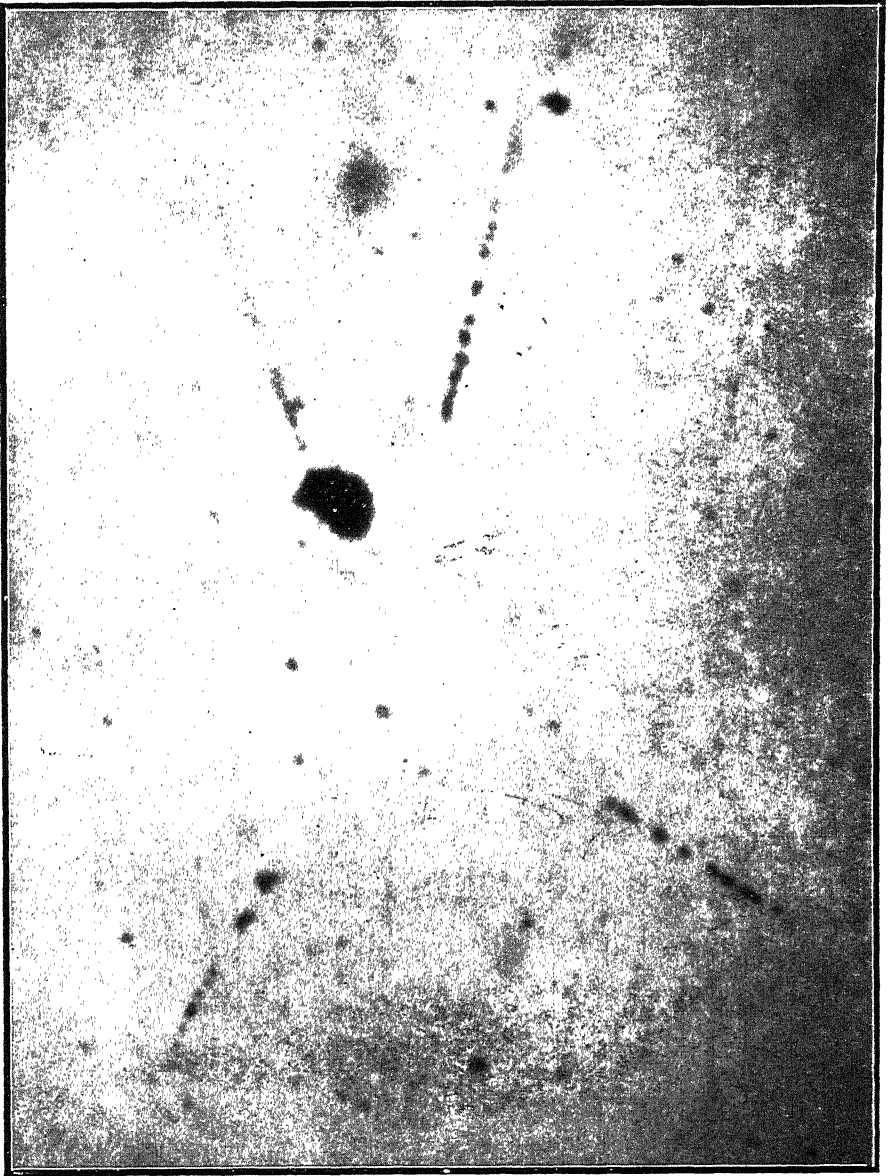
Description of photographs

Fig. 1 Numerous α -particle tracks produced by soaking the plate in a weak solution of Th. (B + C). Magnification 850 \times .



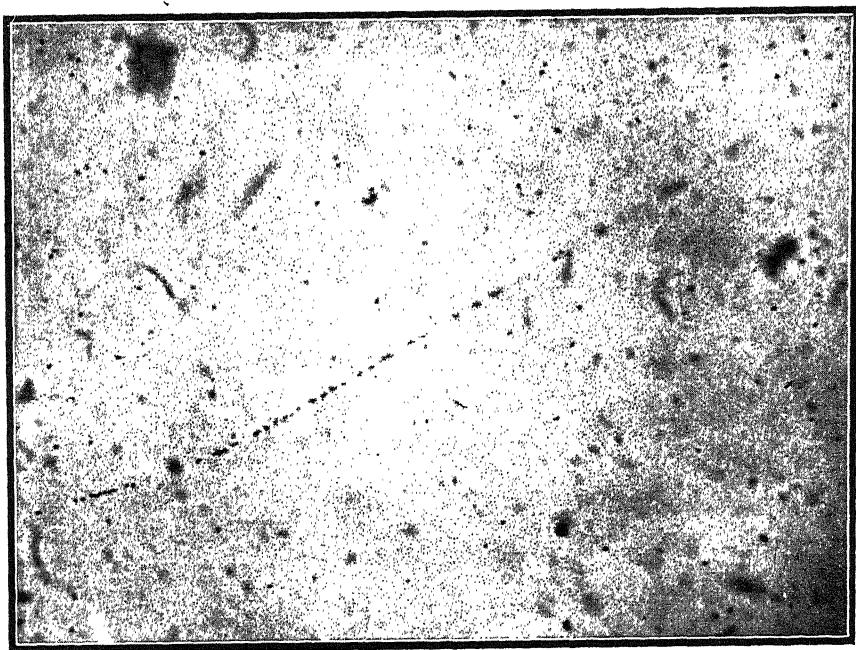
(Figure 1)

Trans. 6: The Tracks of Swift Nuclei in Photographic Emulsions : by Prof. H. J. Taylor



(Figure 2)

Trans. 6: The Tracks of Swift Nuclei in Photographic Emulsions: by Prof. H. J. Taylor.



(Figure 3)

Trans. 6: The Tracks of Swift Nuclei in Photographic Emulsions : by Prof. H. J. Taylor



(Figure 4)

Trans. 6: The Tracks of Swift Nuclei in
Photographic Emulsions : by Prof. H. J. Taylor.



(Figure 5)
Trans. 6: The Tracks of Swift Nuclei in Photographic
Emulsions: by Prof. H. J. Taylor.

Fig. 2 Four α -particle tracks in the emulsion, arising from a radioactive inclusion in the glass. Magnification 2400 \times .

Fig. 3 Track of a proton produced by the passage of a neutron through the emulsion (Process plate). Magnification 600 \times .

Fig. 4 Typical track corresponding to reaction (2). Magnification 3000 \times .

Fig. 5 Tracks corresponding to reaction (1) The separate tracks of the two particles are indicated. Magnification 3500 \times .

ON THE NATURE OF CHEMICAL BINDING OF CERTAIN OXIDES AND SULPHIDES.

By

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I

In recent years there seems to be a good deal of difference of opinion regarding the nature of binding in compounds like the hydrogen halides and some oxides and sulphides, but in most cases proper data which will decide whether a compound is distinctly ionic or atomic are lacking. The present paper is in the nature of a discussion which attempts at proving that the bindings of the compounds ZnS, ZnO, CdS, CdO, HgS, CaO, SrO and BaO, investigated by the author are definitely ionic in nature.

In the case of diatomic compounds, specially the saturated oxides in which the atoms are divalent, some authors assign a structure on the same lines as that assigned to BeO by Mulliken¹. The emission band spectrum of BeO was found to be due to a transition ${}^1\Sigma \rightarrow {}^1\Sigma$. Mulliken postulated that the ground state dissociates in the limit to Be ($s^2 {}^1S$) and O ($p^4 {}^1D$) when the distance between the nuclei is increased to infinity due to vibration energy.

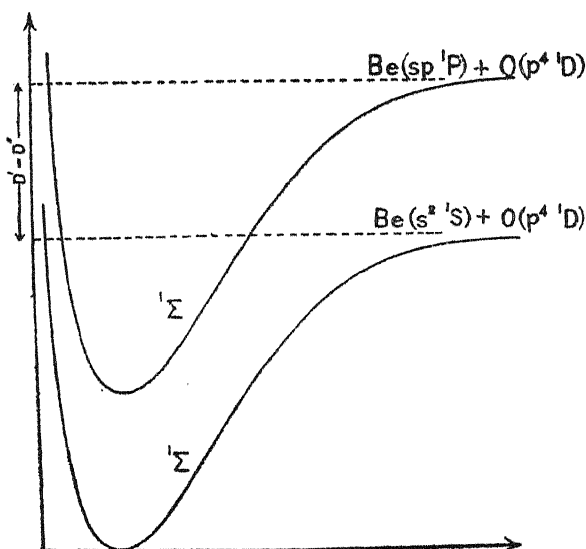


FIG. 4.

Transaction No. 7: on the Nature of Chemical Binding of certain Oxides and Sulphides by P. K. Sen-Gupta.

1. Mulliken, Rev. Mod. Phys. Part III.

We will disregard for the time being the suggestion by Herzberg¹ and others that the chemical linkages formed by the s^2 electrons are unstable.

The state $^1\Sigma$ which results from the foregoing association of BeO explains the diamagnetism of BeO. The excited state which is also a $^1\Sigma$ state dissociates into Be ($sp\ ^1P$) and O ($p^4\ ^1D$), that is, in the process of excitation Be (1S) has been raised to the state Be (1P). The Difference $D' - D''$ between the dissociation continua is claimed to be close to the value of $^1S - ^1P$ of Be, and the closeness is cited by the authors to prove the correctness of their hypothesis. But actually the agreement was not found to be so good as expected, and Lessheim and Samuel² were led to take an altogether different view of the structure of BeO in its ground and excited states. According to these authors, the picture is more like that shown in Fig. 2. They hold that even in the ground state one of the $2s$ electrons in Be is promoted to $2p$, and in the excited state both of them are promoted to $2p$. The value of $D' - D''$ is in better agreement with the energy of promotion $2s2p - 2p$ now.

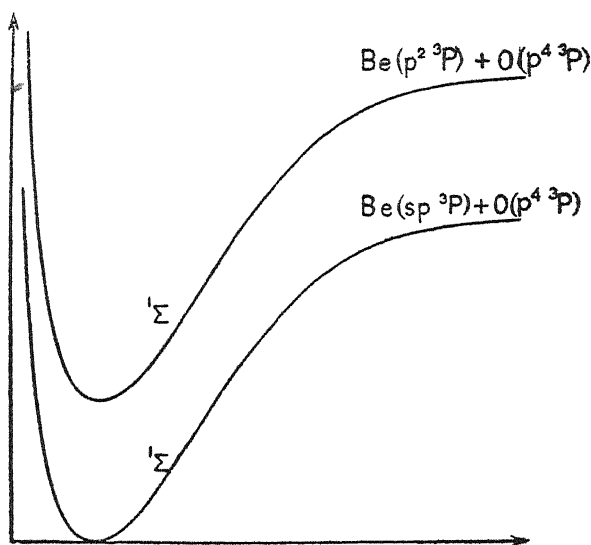


FIG. 2.

Transaction No. 7: On the Nature of Chemical Binding of certain Oxides and Sulphides by P. K. Sen-Gupta.

The application of the foregoing ideas to the sulphides³ and

1. Herzberg, Zeit. f. Phys. Vol. 75. p. 601, 1930
2. Lessheim and Samuel, Zeit. f. Phys. Vol. 84, p. 637, 1933.
3. Sen-Gupta, Proc. Roy. Soc. A., Vol. 143, p. 438, 1934.

oxides¹ of Zn, Cd and Hg receives a check at the very outset. The absorption spectra of the vapours of these substances were studied by the present author, and are reported elsewhere, but no trace of any band absorption was found between λ 8000 and λ 1900. If the theories of Lessheim and Samuel (*loc. cit.*) or of Mulliken (*loc. cit.*) held good the Franck-Condon diagrams of these compounds would be of the type given in Figs. 1 or 2, in which the atoms Be and O can be replaced by, say, Cd and S respectively. On account of the definite absence of band absorption at the expected place, it is clear that neither of the two associations of Cd and S, shown in Figs. 1 or 2 are involved in the ground state.

In all the oxides and sulphides investigated by the present author, not only are the band absorptions absent, but we have to account also for the continuous absorptions obtained. I have found that the vapours of these substances always show a continuous absorption beginning from a long wavelength limit ($h\nu_1$) followed by retransmitted patch of light with second absorption (beginning represented by $h\nu_2$). In the case of HgS, there is a third region of absorption ($h\nu_3$) after another retransmitted patch of light. These different absorptions can always be found, if the calculated limits are within the region of investigation. To account for the continuous absorption on the line of Mulliken's or Lessheim and Samuel's hypothesis, if we suppose, that the binding is of Hund's type a, the molecular states possible out of the combination Be ($s^2\ ^1S$) + O ($P^4\ ^1D$) are $^1\Sigma$, $^1\Pi$, $^1\Delta$ of which the $^1\Sigma$ state is presumably stable. The $^1\Pi$ and $^1\Delta$ states are most likely unstable since no emission band system due to them are known. We will consider here only the transition to the $^1\Pi$ state as the transition to the $^1\Delta$ state is forbidden by the selection principles. A Frank-Condon picture of the repulsive states is shown in Fig. 3. The excited state which is formed out of Be ($sp\ ^1P$) O ($p^4\ ^1D$) has a similar repulsive state $^1\Pi$. Absorption experiments if the picture were true, will reveal continuous absorptions due to



(while $^1\Sigma \rightarrow ^1\Sigma$ should show band absorption). The difference in energies of the first two long wave beginnings of absorptions, that is, $h\nu_1 - h\nu_2$ should then give the value of $^1S - ^1P$ of Be. But it is very difficult to try this experiment with BeO which melts at a very high temperature, and probably gives appreciable vapour pressure at a temperature higher than 2000° C. We have to fall back upon the compounds of Zinc, Cadmium, and Mercury mentioned above which were actually tried by myself.

If we suppose that the compounds investigated by me are built

1. Sen-Gupta, Bull. Acad. Sci. U. P. Vol. 2, p. 245, 1933.

on a similar model, the continuous absorptions should be due to transitions from A to B and C (Fig. 3). The interval between the

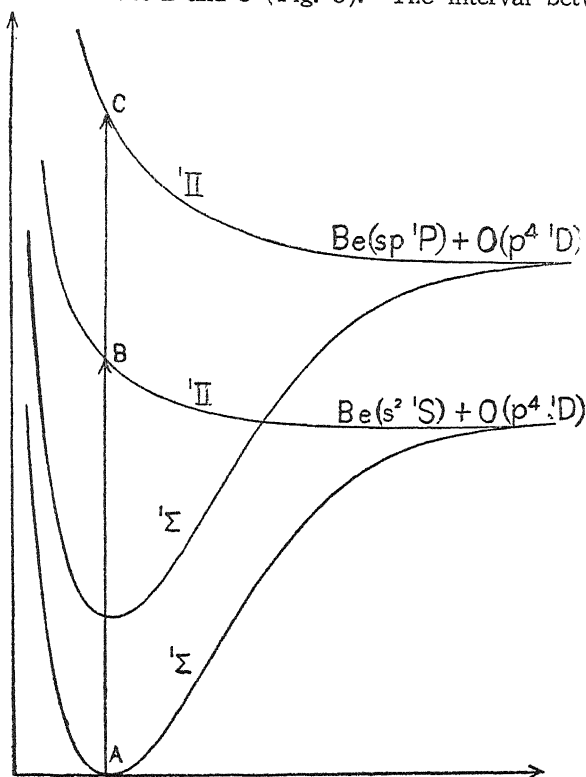


FIG. 3.

Transaction No. 7: On the Nature of Chemical Binding of certain Oxides and Sulphides by P. K. Sen-Gupta.

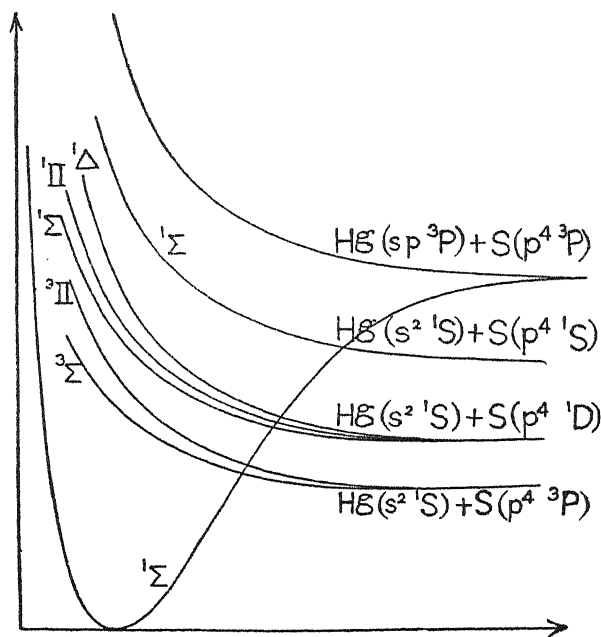
two cuts should equal $s^2\ ^1S - sp\ ^1P$ of Zn, Cd or Hg. But this is far from being the case as shown in the following table.

TABLE I

| Substance | $h\nu_1 - h\nu_2$ | $^1S - ^1P$ of metal |
|-----------|-------------------|----------------------|
| ZnS | 1.3 volts | 5.9 volts |
| CdS | 1.3 volts | 5.4 volts |
| HgS | 1.22 volts | 5.0 volts |

Hence the Mulliken picture fails for the observed absorption spectra of the sulphides as well as oxides of Zn, Cd and Hg.

According to Lessheim and Samuel the linkage with the s^2 electrons of Be (or Zn, Cd and Hg) will give repulsive states only, so that the continuous absorptions may be said to be due to a transition to the repulsive states of the molecules formed by linkages with the s^2 electrons of the metal, as shown in Fig. 4. The ground state is



FIG(4)

Transaction No. 7: On the Nature of Chemical Binding of certain Oxides and Sulphides by P. K. Sen-Gupta.

the same as in Fig. 2. The relative positions of the dissociation continua cannot be fixed with respect to the dissociation continuum of the ground state, the position of which is unknown if the linkage is supposed to be atomic. If there were only one repulsive state due to each metastable state of oxygen or sulphur atom, the three absorptions obtained by myself and their relative differences would be qualitatively explained. But there are in all six repulsive states, transitions to five of which are allowed. And again these should be intermingled with the repulsive states arising out of the combination of the ground state also, so that there would be more than five continuous absorptions mixed up with each other within the region investigated in some cases. The whole idea is too qualitative, and does not possess the simplicity and clearness of the assumption of an ionic binding with the units like Zn^{++} , S^{--} , as shown by the

present author in the papers on the oxides¹ and sulphides of the metals (loc. cit.).

II

In the case of CaO, SrO and BaO calculations showed that only the first absorption beginning was within the quartz region and the second fell in the fluorite region.

Mahanti² and others have investigated the emission band spectra of these compounds and have assigned the bands to the transition $^1\Sigma \rightarrow ^1\Sigma$. Mahanti assumes a picture of BaO similar to that of BeO of Mulliken, that is, in the ground state BaO has the constitution $\text{Ba} (^1\text{S}) + \text{O} (^1\text{D})$ and in the excited state $\text{Ba} (^1\text{P}) + \text{O} (^1\text{D})$. The following points may be put forward against this picture.

1. The band absorption corresponding to the so-called fundamental emission bands are absent, which means, that the ground state is not involved in the production of the emission bands.

2. An unstable state (which can also be present) due to $\text{Ba} (^1\text{S}) + \text{O} (^1\text{D})$ will give continuous absorption, as discussed in Part I of this paper. Since this repulsive state ^1II will have the same dissociation energy as the ground state $^1\Sigma$, the beginning of absorption (continuous) corresponding to transition AB in Fig. 5 will have almost the same energy as the dissociation energy of the ground state, or may be higher.

In the following table the calculated values of Mahanti (loc. cit.) of D' and the experimental values of the beginnings of absorption³ that is, $h\nu$, have been compared.

Table II

| Substance | $h\nu$ | D' |
|-----------|-----------|------------|
| CaO | 6.0 volts | 4.58 volts |
| SrO | 4.8 volts | 1.52 volts |
| BaO | 5.9 volts | 6.32 volts |

There is no agreement at all. In the first two cases we may try to stress the agreement by supposing that the repulsive curve ^1II is not horizontal but rises very steeply,⁴ so that AB (Fig. 5) is almost

1. Sen-Gupta, Bull. Acad. Sci., U. P. Vol. 2, P. 245, 1933.

2. Mahanti, Phys. Rev., Vol. 42, p. 609, 1932.
Proc. Phys. Soc., Vol. 46, p. 51, 1933

3. Sen-Gupta, Bull. Acad. Sci., U. P., Vol. 3, p. 203, 1934.

4. Sen-Gupta, Zeit. f. Phys., Vol. 88, 647, 1934.

double the value of D . But if this were the case, the absorption cut would not be sharp as actually observed in these cases, but would be very gradual as in the case of the hydrogen halides. So this argument fails.

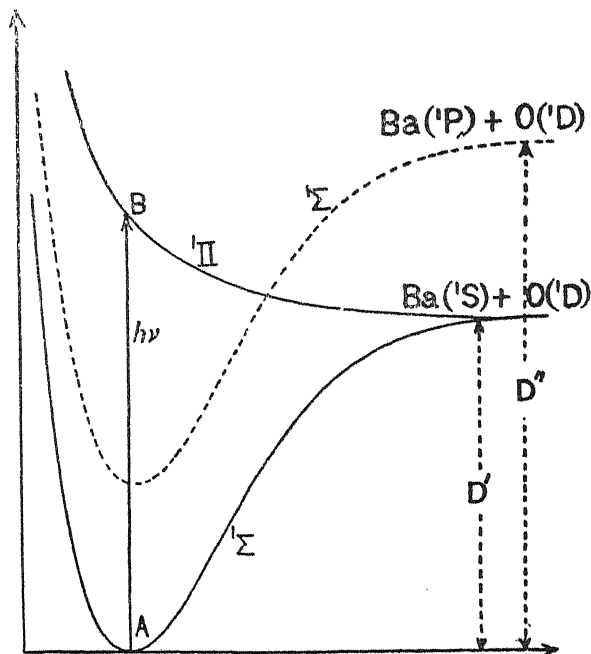


FIG. (5)

Transaction No. 7: On the Nature of Chemical Binding of certain Oxides and Sulphides by P. K. Sen-Gupta.

3. The differences of the dissociation energies. $D' - D''$ in Fig. 1 of two states of BaO which are responsible for the emission bands, are claimed to give the value of $^1S - ^1P$ of Ba by Mahanti, but it has been found that, $D' - D''$ agrees better with the value of $^2S - ^2D$ of Ba^+ . This shows that the emission bands are caused by two intermediate states, which are due to the ionic combination of Ba^+ and O^- , and Ba^+ (excited) and O^- respectively as shown in Fig. 6.

Since the dissociation energies are known it will be possible to ascertain, whether, the continuous absorption obtained by me is due to the transition to repulsive state which is caused by linkage with s^2 electrons of the metal. The ground state which is the stable state should then consist of $Ca(sp^3P) + O(p^4^3P)$ on the lines of Lesheim and Samuel (loc. cit.). There will be two repulsive states due to the combination $Ca(s^2^1S) + O(p^4^3P)$, that is, $^3\Sigma$, $^3\Pi$ having

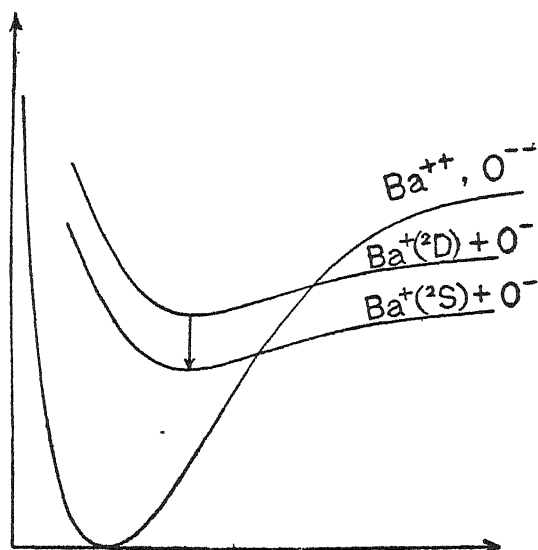


FIG. 6

Transaction No. 7: On the Nature of Chemical Binding of certain Oxides and Sulphides by P. K. Sen-Gupta.

common dissociation energy. The potential energy curves of the repulsive states will cut that of the ground state as shown in Fig. 7.

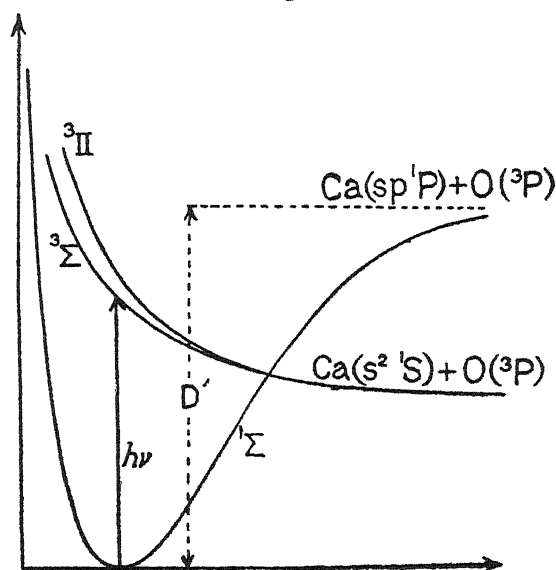


FIG. 7.

Transaction No. 7: On the Nature of Chemical Binding of certain Oxides and Sulphides by P. K. Sen-Gupta.

It is evident that the first beginning of absorption $h\nu_1$ will correspond to an energy which is less than the energy of dissociation D' of the ground state.

From Table II it is seen that in two of the cases, values of $h\nu$, instead of being smaller, are so much greater than those of D' as to make the idea agreement absurd. It has already been pointed out that on account of the sharp absorption cuts we cannot assign a steep inclination to the upper curves so as to give a better agreement between $h\nu$ and D' .

The logical conclusion from the foregoing arguments is that the assumption of an atomic binding for the saturated oxides and sulphides cannot explain the experimental results obtained by the author. On the other hand such an assumption leads to insuperable difficulties. The assumption of an ionic binding, on the other hand explains the results satisfactorily, as shown in the previous papers.

My best thanks are due to Prof. M. N. Saha, D. Sc., F. R. S., for his encouragement in connection with this work. I am also thankful to Dr. Lessheim and Dr. Samuel for some criticisms and discussions.

ON THE THEORY OF VISCOSITY OF LIQUID METALS.

By

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In view of the recent investigations into the properties of liquid metals, it may be of interest to study the phenomenon of the viscosity of metals in the liquid form from the point of view of the electron theory. Following the recent work of Andrade¹ and also of Mott² we take the liquid metal near the melting point as still possessing the lattice structure which was characteristic of it in the solid state—the Debye or rather Einstein characteristic frequency being, of course, different in the liquid state. In fact,

$$\left(\frac{v_L}{v_S}\right)^3 = -\frac{L}{e k T}$$

where L is the latent heat. The formula for the viscosity of liquids deduced by Andrade on the assumption of this continuity of lattice structure may be obtained as follows:—

If m is the mass of a molecule and l is the average distance between the centres of the molecules, the change in momentum in one period is $2 \ m l \ \frac{dv}{dz}$

or the change in momentum per second is $2 \ m l \ \frac{dv}{dz} \ \nu$

where ν is the frequency of vibration of the molecule. If we make the usual simplifying assumption that one-third of the molecules are vibrating along each of the three directions normal to one another, the change in momentum for all molecules in unit area will be:

$\frac{2}{3} N \nu m l \ \frac{dv}{dz}$ where N is the number of molecules per unit area of a layer and is equal to $\frac{1}{l^2}$

Supposing now that the communication of momentum takes place at every extreme libration and that a molecule conveying momentum crosses a plane parallel to the drift twice in every complete vibration, the transfer of momentum per second per unit area is

$$\frac{4}{3} N \nu m l \ \frac{dv}{dz} = \frac{4}{3} \frac{\nu m d}{l} \frac{dv}{dz} = \eta \frac{dv}{dz}$$

Hence

$$\eta = \frac{4}{3} \frac{\nu m}{l}$$

Substituting for ν from Lindemann's formula³,

$$\nu = C \sqrt{\frac{T_m}{A V_A^{2/3}}}$$

where ν is the fundamental frequency, T_m is the melting point, A , the atomic weight and V_A the volume of a gram-atom at temperature T_m , we get,

$$\eta = \frac{4}{3} \frac{m}{l} C \sqrt{\frac{T_m}{A V_A^{2/3}}}$$

Since

$$l = \left(\frac{V_A}{N}\right)^{1/3} \text{ and } m = \frac{A}{N}$$

where N is Avogadro's number, we obtain,

$$\eta = \frac{4}{3} C \frac{(A T_m)^{1/2}}{(N V_A)^{2/3}} = 5.1 \times 10^{-4} \frac{(A T_m)^{1/2}}{(V_A)^{2/3}} \dots (1)$$

for $C = 2.8 \times 10^{12}$ and $N = 6.06 \times 10^{23}$

This is Andrade's formula for the viscosity of liquids.

The Debye frequency ν in the relation $\eta = \frac{4}{3} \frac{\nu m}{l}$ may however be expressed with advantage in terms of the Debye temperature θ_L as is more usual with workers in modern Physics and perhaps theoretically better than expressing it in terms of the melting point temperature T_m . In view of the imperfect knowledge of the behaviour of adjacent layers and molecules of liquids and of the average distance by which a molecule leaves its position of equilibrium it may also be safer to introduce a constant β in the relation between l and n and put $\beta l = n^{-1/3}$ where n is the number of molecules per unit volume. We then get,

$$\eta = \frac{4}{3} \beta \nu m n^{1/3}$$

If ρ denotes the density, A , the atomic weight and m_H the mass of the hydrogen atom, we have,

$$n = \frac{\rho}{A m_H} \text{ and } \eta = \frac{4}{3} \beta \nu \left(\frac{\rho}{A}\right)^{1/3} A m_H^{2/3}.$$

Putting

$$h\nu = k\theta_L \text{ or } \nu = \frac{k}{h}\theta_L$$

where k represents Boltzmann's constant, h is Planck's constant and θ_L is the Debye characteristic temperature, we have,

$$\eta = \frac{4}{3} \beta \frac{k}{h} m_H^{2/3} A \left(\frac{\rho}{A}\right)^{1/3} \theta_L \dots \dots \dots (2)$$

Both the formulae (1) and (2) express the viscosity in terms of experimental constants having nothing to do with viscosity measurements.

We can now compare the values of viscosity calculated from the above theoretical formulae (1) & (2) with the observed values of

viscosity of certain liquid metals for which published experimental data exist.

Table giving the calculated and observed values of viscosity of liquid metals.

| Liquid metal | η cal. from (1) | η cal. from (2) with $\beta = 2.3$ | η obs. |
|--------------|----------------------|---|-------------|
| Cd | | 0.024 | >0.018 |
| Hg | 0.021 | 0.023 | 0.021 |
| Cu | 0.038 | 0.032 | 0.038 |
| Sn | 0.019 | | 0.020 |
| Pb | 0.025 | 0.023 | 0.028 |

It will be seen from the above table that the agreement between the values calculated from (2) and the observed values is fairly satisfactory considering the uncertainty⁴ about the experimental results obtained by different workers. The values calculated from (1) are, no doubt, in extraordinarily close agreement with the observed values but this seems to be more or less a chance coincidence. For, in view of the approximate nature of the assumptions and also the discrepancies in the values of viscosity obtained by various observers⁵, one cannot legitimately expect an agreement within 5 or 10 percent. The values obtained from formula (2) depend upon the value of the constant β which takes account of the crystal structure of the metal. Formula (2) has the additional advantage that it expresses the frequency ν in terms of the Debye characteristic temperature θ_L which is more in keeping with the modern tendency⁶ in theoretical physics and perhaps better than putting ν in terms of the melting point T_m .

The above theory applies rigorously to the viscosity of monatomic metals. The problem of diatomic molecules is therefore left untouched for the present.

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- (2) Mott, Proc. Roy. Soc., 1934, 146, 465
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- (4) Andrade, Phil. Mag. 1934, 17, foot-note on P. 508
- (5) Andrade, loc. cit.
- (6) Mott, loc. cit.

ON THE MAGNETIC MOMENT OF THE NUCLEUS AND
HYPERFINE STRUCTURES IN THE SPECTRUM OF
DOUBLY IONIZED ANTIMONY WITH A NOTE ON
THE STRUCTURE OF THE ARC LINE $\lambda 3723$.

BY

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Summary :

Hyperfine structures of two doublets of the spectrum SbIII have been studied and an approximate value for the magnetic moment of the nucleus derived. A discussion of this has led to a modification of the gross structure analysis. The structure of the arc-line $\lambda 3723$ has been interpreted taking the mechanical moment of the nucleus $= (5/2) h/2 \pi$ for both isotopes.

Introductory :

It is now well known that many spectral lines which appear sharp when examined with spectroscopes of ordinary resolving power split up into a number of components when high resolving power is available. The fact that atoms of the same element have different atomic weights sometimes contributes for some reasons to this so-called hfs* of lines, the effect varying for individual spectral lines. But even simple atoms do show such structures. It was further found that these structures in the favourable cases showed a multiplet form similar to the ordinary multiplets of the gross structures but in a miniature form and it was also found that Lande's interval rule was obeyed for this term-splitting as well. Ruark and Chenault¹, in order to explain this, for the first time introduced one more quantum number F besides the already existing N, L, S and J. Pauli² assigned to the nucleus a favoured direction. With this was associated a definite magnetic moment and hence, just as in the case of the spinning electron, a definite mechanical moment $Ih/2 \pi$, corresponding to a nuclear spin quantum number I. The magnetic moment interacts with the extra nuclear electrons. Thus the total angular quantum number J combines vectorially with I giving rise to the fine quantum number F. The original single energy level characterised by J splits up into $2J+1$ (or $2I+1$, if J is greater than I) levels characterised by definite F values. For the gross structure the mechanical moment

* hfs stands throughout for hyperfine structures.

for a particular state arising from a definite electronic configuration is given by J expressed in units $h/2\pi$ and the magnetic moment is given by $J.g$ expressed in terms of Bohr-magnetons, i. e. $eh/4\pi mc$ units m being the mass of the electron. Here, g is the well known Lande-factor which can be theoretically calculated and derived from the Zeeman effect data. The corresponding ratio of the magnetic moment of the nucleus, expressed in units $eh/4\pi Mc$ or proton-magnetons M being the mass of the proton, to its mechanical moment, expressed in units $h/2\pi$, is known as the $g(I)$ factor. This can be calculated from observed hfs with the aid of mathematical formulae derived by Goudsmit³.

Antimony has two isotopes of atomic weight 121 and 123, their abundance ratio being 100 : 78.5⁴. From a study of the hfs of the lines of the first spark spectrum by the author⁵ their nuclear spin-moments were found to be $5/2$ for Sb^{121} and $7/2$ for Sb^{123} . These were further utilised in explaining the structures of the arc lines⁶. Crawford and Bateson⁷ have corroborated the above values of the spin-moments from their observations of the hfs of the lines of the trebly-ionized atom. Later, however Tolansky⁸ studied the hfs of some lines of the first spark spectrum using a cooler source and concluded that $I = 5/2$ for Sb^{123} as well.

Experimental :

In the present investigation the source used was a quartz discharge-tube which could be evacuated by means of a mercury-pump and filled with helium at low pressure as desired. Metallic antimony was kept in the bulbs of the discharge-tube and heated. A sketch of the discharge-tube is given in Fig. 1. A condensed discharge was passed through the capillary portion of the tube, 4 cm. long and 1.5 mm. in diameter, and excited the SbIII lines quite strongly. For investigating the hfs a Fabry-Perot etalon was placed in the parallel beam of light between the collimator and the prisms of a Zeiss-constant-deviation three-prism glass spectrograph for which the average dispersion in the region investigated was 8.8 Å. U. per mm. Invar rings of suitable thicknesses, inserted between the two quartz plates of the etalon, served to give the desired dispersion for the hfs.

The wave-lengths of the four lines selected for a study of their hfs are given below in column 1 of Table I and their classifications⁹ in column 2. The observed hfs were diffuse but each line was clearly resolved as a doublet, the component to the longer wave-length being the stronger of the two. The visually estimated intensities of the components are in the ratio of about 4 : 3. Separations of the two components for the respective lines are given in wave-numbers

to two places of decimals in column 3 of the Table, the separations being measured between points of maximum intensities of the components.

Photographs of the fringes of the four lines given in the Table are reproduced in plate I, A, B, C, D. A and B are taken with a gap of 2mm. between the etalon plates, while C and D are taken with a 3mm. gap corresponding to dispersions 2.5ν and 1.6ν respectively per order.

TABLE I.

| λ I. A. | Classification. | Separation. $\Delta\nu$ |
|-----------------|---|-------------------------|
| 4265.09 | (5s. ² 6s.) $^2S_{\frac{1}{2}} - (5s.2 6p.) ^1P_{\frac{3}{2}}$ | 1.27 |
| 4591.89 | (") " - (") $^2P_{\frac{1}{2}}$ | 1.40 |
| 4352.16 | (5s.5p. ²) " - (") $^1P_{\frac{3}{2}}$ | 0.45 |
| 4692.91 | (") " - (") $^1P_{\frac{1}{2}}$ | 0.55 |

Discussion.—It is of course not possible to throw any further, light on the values of the nuclear spin moments from the available data. Theoretically we should expect $\lambda\lambda$ 4265 and 4352 to be split up into six components corresponding to each isotope i.e. either line should show twelve components. $\lambda\lambda$ 4592 and 4693 should similarly show eight components each. In Fig. 2 are given the very useful graphical pictures¹⁰ of what the components would look like for the transitions ... (a) $^2S_{\frac{1}{2}} - ^2P_{\frac{3}{2}}$ and (b) $^2S_{\frac{1}{2}} - ^2P_{\frac{1}{2}}$, for the isotope Sb¹²¹. The intersections of any horizontal line with the graph would give the relative positions of the components for a definite ratio of the splitting factors of the combining terms. At the centre, only the 2S splitting would be responsible for the structure, the splitting factor for the 2P term being zero i.e. corresponding to the ratio 1:0. The top and the bottom correspond to the ratios 1: + 1 and 1: - 1 respectively. The theoretically calculated relative intensities¹¹ of the components are given at the bottom. The thick lines give the mean positions of the unresolved components due to the 2P term-splitting. It is evident that a comparatively small splitting of the 2P terms would show the structures as doublets. Further, a similar but narrower structure would be superposed on this due to the second isotope, its I-value being taken equal to 5/2. It can be concluded

from the observed patterns that the $6s\ ^2S$ term has the largest splitting factor, next comes the $(5s\ 6p^2)\ ^2S$ term, while the $6p\ ^2P$ terms have small but positive factors that of $^2P_{\frac{3}{2}}$ being smaller of the two. Giving the $^2P_{\frac{3}{2}}$ term a small negative factor would lead us to assign a comparatively large value for the $^2P_{\frac{1}{2}}$ splitting which would not be compatible with the observed data. The resultant term-splitting for the two isotopes would be about $1.38\ \nu$ and thus the splitting for the $6s\ ^2S$ term for the lighter isotope* would be about 1.58 , which gives for the splitting factor a value $A = 0.53\ \nu$ approximately. The corresponding factors for the $6p\ ^2P$ terms would be the order of 0.02ν .

For calculating the $g(I)$ factor from the splitting of a term, arising from a single outer s-electron, Goudsmit³ gives the following formula :

$$(I) = \left[\frac{3A \cdot n_o^3 \cdot 1838}{8R \alpha^2 \cdot Z_i \cdot Z_o \cdot K(\frac{1}{2}, Z_i)} \right], \text{ where } K(J, Z_i) = 4J(J + \frac{1}{2})(J + 1)/(4\rho^2 - 1)\rho.$$

and $\rho^2 = (J + \frac{1}{2})^2 - (\alpha \cdot Z_i)^2$. Here, n_o is the effective total quantum number and could be calculated from a knowledge of the absolute term-value. For SbIII, Lang⁹ gives for the $6s^2S$ term a value 107321 , and for the $5s5p^2\ ^2S$ term 106852 , based on an arbitrary choice of $64000\ \text{cm}^{-1}$ for the $5f\ ^2F_{\frac{7}{2}}$ term. Corresponding to the term value $107321\ \text{cm}^{-1}$, $n_o = 3.034$. Z_o is the effective nuclear charge for a hydrogenic orbit, and in the case of a doubly-ionized atom, therefore, is equal to three. Z_i is the effective nuclear charge for a penetrating orbit and for an s-electron $Z_i = Z = 51$ for antimony. R is the Rydberg constant and α is the fine-structure constant $= 2\pi e^2/hc$. The $g(I)$ value on calculation comes out to be about 2.88 units and the corresponding magnetic moment is about 7.2 proton-magnetons for Sb^{121} . Goudsmit³ has calculated the magnetic moments from the author's hfs data for the SbII lines. He obtains the value 2.7 for Sb^{121} and 2.1 for Sb^{123} , corresponding to the $g(I)$ values 1.1 and 0.6 respectively. Breit and Wills¹² by a more detailed theoretical consideration obtain the value 1.3 instead of 1.1 . It is interesting to note that taking the ratio of the $g(I)$ factors of Sb^{121} and Sb^{123} as 1.37 , as given by Tolansky⁸, and the I -value as $5/2$ for both, corresponding to the value 2.7 for Sb^{121} the magnetic moment for Sb^{123} comes out to be 2.0 , not differing much from the value already quoted above. The value 7.2 , as here obtained, is no doubt not very exact; nevertheless, it shows that the formula

* Calculated from the known ratio of the abundance of the two isotopes and the ratio of their $g(I)$ factors.

applied to the hfs of the lines of the doubly-ionized atom gives rather too high a value.

The abnormal value obtained is in the author's opinion due to an improper classification of the gross structure of the SbIII spectrum. If the $6s\ ^2S$ term is interchanged with the $5s\ 5p^2\ ^2S$ term, the $g(I)$ value deduced is very near the value obtained by Goudsmit and the large splitting thus assigned to the $5s\ 5p^2\ ^2S$ term (as modified) is also not unexpected. In fact, in a previous classification Lang¹³ put the $6s\ ^2S$ term higher than the $5s5p^2\ ^2S$ term, but later, in order to bring the classification in consonance with that of As III, he put the higher term as $5s5p^2\ ^2S$ and the lower as $6s\ ^2S$ However, a comparison of the relative intensities of the two doublets supports the modification. The transition $s\ ^2S \leftarrow p\ ^2P$ should be more probable than the transition $s\ p^2\ ^2S \leftarrow p\ ^2P$ which involves a double electron-transition. The latter should therefore be expected to be weaker in intensity. Of the two doublets of the spectrum Sb III that to the longer waves is decidedly the stronger and should therefore involve the $s\ ^2S$ term which substantiates the above modification. For the spectrum As III on the other hand, the doublet to the shorter waves is the stronger and this is in accord with the existing classification. A study of the hfs of the corresponding lines of the spectrum As III has now been undertaken and would help to decide the question. Further, in support of this modification it may be noted that in the spectra SeIV¹⁴ and TeIV¹⁵, iso-electronic with AsIII and SbIII respectively, the $s\ ^2S$ term is higher than the $p^2\ ^2S$ term. In Table 2 are given the absolute term-values for GaI-like and InI-like spectra for the two terms in question, those for SbIII being modified as suggested above. The term-values for the first spark spectrum are divided by four, those for the second spark spectrum by nine and so on, for better comparison. As is seen from the Table, the change in the relative term-magnitudes of the $s\ ^2S$ and $p^2\ ^2S$ terms is quite gradual from the arc spectrum to that of the trebly-ionized atom.

TABLE 2.

| Spectrum | Term-values | | Spectrum | Term-values | |
|----------|-------------|---------------|----------|-------------|---------------|
| | $5s\ ^2S$ | $4s4p^2\ ^2S$ | | $6s\ ^2S$ | $5s5p^2\ ^2S$ |
| Ga I | 23592 | 8115 | In I | 22295 | — |
| Ge II | 16559 | 13586 | Sn II | 15204 | 8996 |
| As III | 13524 | 13400 | Sb III | 11872 | 11925 |
| Se IV | 11803 | 13582 | Te IV | 10727 | 12222 |

Taking the previously accepted $5s5p^2\ ^2S$ term, then, as the real $6s\ ^2S$ term, the resultant term-splitting for the two isotopes would be about $0.52\ \nu$. This gives for Sb^{121} , for the $6s\ ^2S$ term, a splitting about $0.60\ \nu$ corresponding to the splitting factor $A = 0.20$. Taking the absolute term-value = 106852, the effective quantum number $n_0 = 3.040$. Substituting these in the $g(I)$ formula we get $g(I) = 1.1$ approximately, rather in too good an agreement with the value given by Goudsmit. The corresponding magnetic moment for Sb^{121} would be 2.7 proton-magnetons.

Structure of $\lambda\ 3723$:

The structure of this particular arc-line $\lambda\ 3723$, ($5p^3\ ^2P_{\frac{3}{2}} - 5p^2\ 6s\ ^4P_{\frac{1}{2}}$), was explained in detail by the author in a previous publication.⁶ The separations of the observed positions of its six components in $10^{-3}\ \text{cm}^{-1}$ were given as follows: 0, (9); 98, (8); 250, (10); 470, (3); 615, (8); and 724, (9). The figures in brackets give the visually estimated intensities. Of these six components the middle two are blends. The structure was explained by taking the I -values $5/2$ and $7/2$ for Sb^{121} and Sb^{123} respectively. The structure could also be explained fairly satisfactorily taking $I=5/2$ for Sb^{123} as well, as given by Tolansky⁸, whose deduction is entitled to more weight on score of a better source. The ratio of the $g(I)$ factors could be calculated by taking the ratio of the separations between the first and the last and the second and the fifth components and comes out to be 1.4 , which is in very good agreement with 1.37 derived by Tolansky. The interval factors, expressed in $10^{-3}\ \text{cm}^{-1}$, for the $5p^3$ term are 162 and 116 and for the $5p^2\ 6s$ term 79 and 56 for Sb^{121} and Sb^{123} respectively. The observed positions of the two unresolved middle components are very near the calculated positions of their resultants. The structure calculated from the above interval factors is given below in Table 3. Figures enclosed in brackets give the calculated¹¹ relative intensities of the components.

TABLE 3.

| Isotope | Calculated structure in unit $10^{-3}\ \text{cm}^{-1}$ | | | | Centre of gravity. |
|---------|--|-------------|-------------|-------------|--------------------|
| 121 | 0 (70) | 237 (56) | 487 (20) | 724 (70) | 341 |
| 123 | 98 (56) | 266 (45) | 447 (16) | 615 (56) | 341 |

A comparison of the observed structure (a) with the calculated structure (b) is given in Fig. 3. The lengths of the lines represent the intensities,

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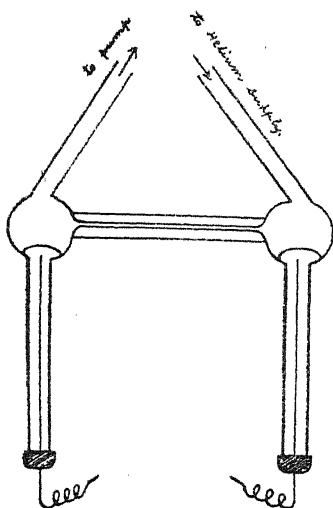


Fig. 1

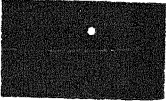


Plate ID



Plate IA



Plate IB



Plate IC

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etc. by J. S. Badami.

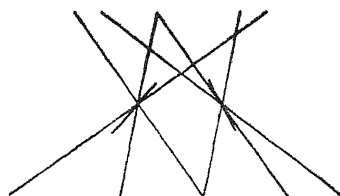


Fig. 2-(a).

Transaction No. 9: On the Magnetic Moment of the Nucleus and Hyperfine
etc. by J. S. Badami.



Fig. 2-(b).

Transaction No. 9: On the Magnetic Moment of the Nucleus and Hyperfine
etc. by J. S. Badami.

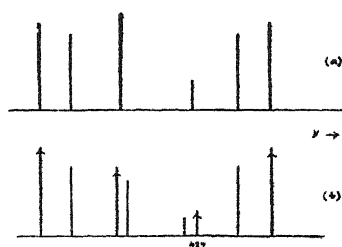


Fig. 3.

Transaction No. 9: On the Magnetic Moment of the Nucleus and Hyperfine
Structures in the Spectrum of Doublyionized Antimony with a note on
the Structure of the Arc Line by J. S. Badami.

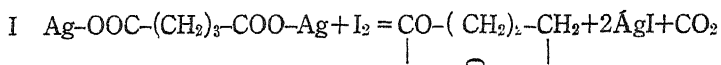
A STUDY IN THE DEGRADATION TO SUCCINIC ACIDS
THROUGH γ -BUTYRO-LACTONES AND OTHER RE-
ACTIONS OF β -ANISYL AND β -HALOGEN-
ANISYL GLUTARIC ACIDS.

BY

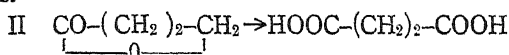
DATTATRAYA BALKRISHNA LIMAYE and RAGHUNATH GANESH CHITRE.

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During the investigation on Cholesterin, Windaus has obtained substituted glutaric acids as degradation products, and for the identification of these, a method was developed by Windaus and Klänhardt, (B. 54, 581-587) depending upon the action of iodine on the silver salts, when the γ -butyro-lactones are formed.



These lactones when oxidised give rise to the corresponding succinic acids.

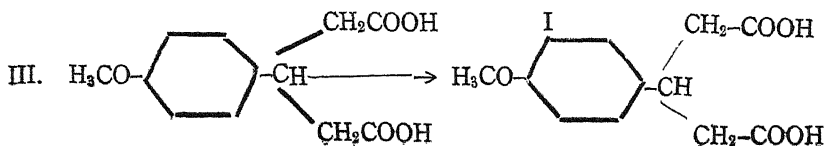


This reaction as regards β -substituted glutaric acids has been tried on alkyl substituted acids only.

Hence a study of the degradation of β -aryl-glutaric acids to the corresponding succinic acids through γ -butyro-lactones was undertaken and as a representative of the class of β -aryl glutaric acids, β -(4-methoxy-phenyl)-glutaric acid was chosen.

However as the work progressed it was found necessary to include β -(Halogen-anisyl)-glutaric acids also. Moreover the condensations of the ethyl-esters of the new glutaric acids with oxalic-ester (Dieckmann, B. 32, 1930-35; 1899) have been studied and a number of functional derivatives have also been prepared.

When the silver salt of β -(4-methoxy-phenyl)-glutaric acid was heated with iodine the corresponding γ -butyro-lactone could not be obtained and a side reaction consisting in the substitution of iodine in the benzene ring took place.

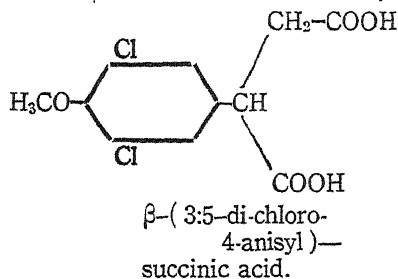
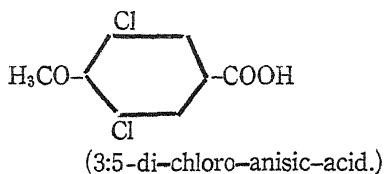
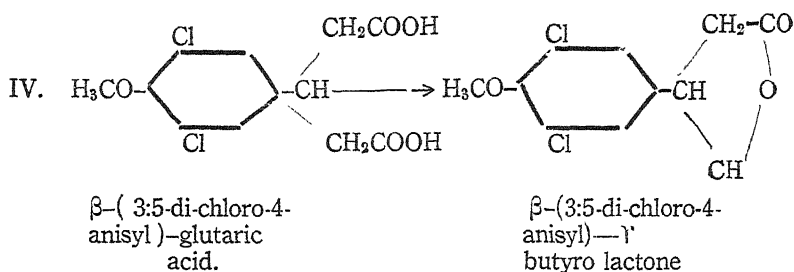


The reaction was then tried on β -phenyl-glutaric acid but in this case also the expected lactone was not obtained.

The β -(Halogenated-aryl)-glutaric acids were next tried. These acids were prepared by the halogenation of the β -(4-methoxy-phenyl)-glutaric acid.

In all, five halogenated acids were obtained namely β -(3-chloro-4-anisyl), β -(3-bromo-4-anisyl), β -(3-iodo-4-anisyl), β -(3:5-dichloro-4-anisyl), and β -(3:5-dibromo-4-anisyl)-glutaric acids.

The position of the halogens in the case of the mono-halogenated acids was determined by the direct oxidation to the corresponding known anisic acids; while in the case of the dihalogenated acids they were determined indirectly by the oxidation of the intermediate γ -butyro-lactones when the corresponding known anisic acids were obtained along with the new succinic acids.

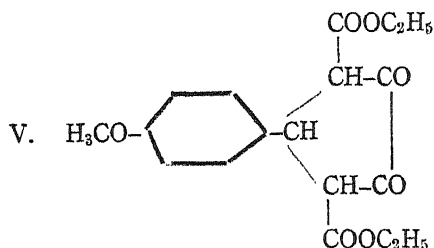


The degradation reaction on the mono-halogenated acids did not give the corresponding lactones while β -(3:5-di-bromo) and β -(3:5-di-chloro)-4-anisyl-glutaric acids gave the corresponding lactones (IV).

These lactones were further oxidised to β -(3:5-di-bromo) and β -(3:5-di-chloro)-4-anisyl-succinic acids, identical with those

obtained by halogenating β -(4-anisyl)-succinic acid prepared by Lapworth's method (Soc. 127, 560-567.); however an attempt to condense 3:5-di-bromo anisaldehyde with sodium-cyan-acetate to form (3:5-di-bromo-4-anisyl)-cyan-acrylic-acid, by Lapworth's method was not successful.

In the case of the condensation of the ethyl-esters of the glutaric acids with oxalicester to form compounds of the type (V), it was necessary to replace dry sodium ethoxide by finely divided sodium.



Di-ethyl-2-(4'-anisyl)-4:5 diketo-pentamethylene 1:3-dicarboxylate.

Owing to the peculiar behaviour of β -(4-methoxy-phenyl)-glutaric acid, in giving the γ -butyro-lactones, only when two halogens are present in the benzene ring, it is intended to investigate the reaction in the presence of other negative substituents.

EXPERIMENTAL.

1. β -(4-Methoxy-phenyl)-glutaric acid (*m. p.* 164°C), the starting material of the investigation was obtained by the reduction with sodium amalgum of β -(4-methoxy-phenyl)-glutaconic acid (Limaye and Bhawe, J. Ind. Chem. Soc. 8, 137; 1931.)

2. β -(4-Methoxy-3-iodophenyl)-glutaric acid (*m. p.* 161°C). Following the method of Windaus and Klänhardt a mixture of 5 Gms. of silver salt of β -(4-methoxy-phenyl)-glutaric acid, 3 Grams of iodine, and 8 Gms of sand was heated for one hour in an oil bath at 150°C. The cooled reaction mass was extracted with ether and the ethereal solution was washed with dilute sodium-carbonate solution. The ethereal solution, on evaporation did not give the expected γ -butyro-lactone, but the carbonate solution on acidification gave a product, which on crystallization from hot water melted at 160°C. Yellow needles, soluble in alcohol and ether, insoluble in benzene. Analysis:—

Found—I = 34.8 per cent. ; Equivalent = 180

C₁₂ H₁₃ O₅ I requires I = 34.9 per cent. ; „ 182

The constitution of this acid, as β -(3-iodo-4-methoxy-phenyl)-glutaric acid was proved by its oxidation to 3-iodo-anisic acid as in (III).

This acid is, however, more conveniently prepared by the following method :—

A mixture of 5 Gms. of β -(4-methoxy-phenyl)—glutaric acid, 2.5 Gms. of iodine, 1 Gm. of iodic acid and 25 c.cs. of water is heated in a sealed tube over a boiling water bath for eight hours. The mixture is then cooled, the contents are transferred to a shallow dish and the excess of iodine is evaporated on water bath. The neutralised solution of the crude acid is treated with barium chloride and is boiled till a considerable reduction in volume occurred, when the insoluble barium salt is precipitated. This, on treatment with hydrochloric acid gives pure acid m. p. 161°C , identical with that obtained by the silver salt method. Yield 4.2 Gms.

Barium salt :—

Found—Ba = 47.43 per cent.

$\text{C}_{12}\text{H}_{11}\text{IO}_5\text{Ba}$, requires—Ba = 47.46 per cent.

3. *3-Iodo-anisic acid* :—5 Gms. of β -(3-iodo-4-methoxy-phenyl)—glutaric acid from (2) were boiled with 25 c. cs. of 10 per cent potassium bi-chromate and 3 c. cs. of con. sulphuric acid on a sand bath under a reflux condenser for half an hour. The solid, that separated on cooling, was dissolved in sodium bi-carbonate solution; on acidification the acid separated, which on crystallization from dil. acetic acid melted at 234°C . Soluble in benzene, alcohol, and acetic acid. Insoluble in water.

It gave no depression in melting point when mixed with the known 3-iodo-anisic acid (B. 17, 2533, 1884.)

4. β -(3-Bromo-4-methoxy-phenyl)—glutaric acid (m. p. 147°C) :—3 Gms. of β -(4-methoxy-phenyl)—glutaric acid were dissolved in 40 c.cs. of ether and to this solution was added 1 c.c. of bromine dissolved in ether. The mixture was allowed to stand for six hours. The insoluble solid which separated was washed with benzene and when recrystallized from hot water melted at 147°C . Yield 1.3 Gms. Soluble in alcohol, ether and dil. acetic acid. Insoluble in benzene. Analysis :—

Found —Br = 25.1 per cent. Equivalent = 158.

$\text{C}_{12}\text{H}_{13}\text{O}_5\text{Br}$ requires Br = 25.2 „ „ „ = 158.5

From the ethereal mother liquor a further yield of 0.4 Gms. of slightly impure β -(3-bromo-4-methoxy-phenyl)—glutaric acid could be recovered.

Barium salt — Found Ba = 30.2 per cent.

$\text{C}_{12}\text{H}_{11}\text{O}_5\text{Br.Ba}$ requires Ba = 30.3 „ „

5. *3-Bromo-anisic acid* :—(m. p. 217°C .) 1 Gm. of β -(3-bromo-4-methoxy-phenyl)—glutaric acid was oxidised by 3 Gms. of potassium bichromate, 2 c.cs. of con. sulphuric acid, and 40 c.cs. of

water as in (3). The pure acid melted at 217°C and was identical with the known 3-bromo-anisic acid prepared by directly brominating anisic acid (Annalen, 56,311).

6. β -(3-Chloro-4-methoxy-phenyl)—glutaric acid. (*m.p.* 157°C):—1 Gm. of β -(4-methoxy-phenyl)—glutaric acid was dissolved in 20 c.cs. of glacial acetic acid and chlorine gas generated from 1 Gm. of MnO_2 , 1 Gm. of NaCl and 4 c.cs. of con. sulphuric acid was passed through the solution. The acetic acid was then evaporated off on water bath and the crude acid was purified through its barium salt. *Mp.* 157°C . Yield 0.6 Gm. soluble in alcohol, ether, and acetic acid. Insoluble in benzene.

Analysis:— Found $\text{Cl} = 11.85$ per cent. Equivalent = 136

$\text{C}_{12} \text{H}_{13} \text{O}_5 \text{Cl}$ requires $\text{Cl} = 12.15$ „ „ „ = 136.3

Barium salt:— Found $\text{Ba} = 33.0$ per Cent.

$\text{C}_{12} \text{H}_{11} \text{O}_5 \text{Cl Ba}$ requires $\text{Ba} = 33.5$ „ „

7. 3-Chloro-anisic acid (*m.p.* 215°C):—It was prepared as in (3) from β -(3-chloro-4-methoxy-phenyl)—glutaric acid. It melted at 215°C and was found identical with the known 3-chloro-anisic acid obtained by chlorinating anisic acid (B. 17,2529).

8. β -(3:5-Dichloro-4-methoxy-phenyl)—glutaric acid. (*m.p.* 194°C):—1 Gm. of β -(4-methoxy-phenyl) glutaric acid was dissolved in 30 c.cs. of glacial acetic acid and a slow current of chlorine gas was passed through the solution for two hours. When the solution was saturated with the gas and assumed a yellow colour, the acetic acid was evaporated on water bath and the residue was boiled with water to remove soluble impurities. The insoluble dichloro-compound, when recrystallized from acetic acid melted at 195°C . Yield 0.8 gm. Insoluble in water and in benzene. Soluble in alcohol and in acetic acid.

Analysis:— Found $\text{Cl} = 23$ per cent. Equivalent = 152.8

$\text{C}_{12} \text{H}_{12} \text{O}_5 \text{Cl}_2$ requires $\text{Cl} = 23.1$ „ „ „ = 153.5

Barium salt:— Found $\text{Ba} = 30.9$ „ „

$\text{C}_{12} \text{H}_{10} \text{O}_5 \text{Cl}_2 \text{ Ba}$ requires $\text{Ba} = 30.9$ „ „

9. β -(3:5-Dichloro-4-methoxy-phenyl)— γ -butyro-lactone. (*mp.* 72°C):—5 Gms. of the silver salt of β -(3:5-dichloro-4-methoxy-phenyl)—glutaric acid were treated with iodine as in (2). The ethereal solution after being extracted with sodium carbonate was evaporated. The semi solid residue, on being treated with deci-normal caustic alkali soon solidified. The solid on re-crystallization from dil. alcohol melted at 72°C . Soluble in benzene, ether, acetic acid. Insoluble in water and dil. alkalis. It dissolved in boiling caustic alkalis but is reprecipitated unchanged on acidification. Yield 0.62 Gm.

Analysis:— Found $\text{Cl} = 27.3$ per cent.

$\text{C}_{11} \text{H}_{10} \text{O}_3 \text{Cl}_2$ requires $\text{Cl} = 27.1$ „ „

The compound resembled the γ -Butyro-lactones⁷ described by Windaus in its properties.

10. β -(3:5-Di-chloro-4-methoxy-phenyl)-succinic acid (*m.p.* 173°C.)—

Method 1:—1 Gm. of β -(3:5-di-chloro-4-methoxy-phenyl)- γ -butyro lactone was oxidized by 0.6 Gm. of potassium bichromate, 40 c.cs. of water and 1 c.c. of strong sulphuric acid on a boiling water bath for two hours. The solid that separated on cooling was dissolved in sodium bicarbonate solution and reprecipitated by acidification and crystallized from hot water, when two substances were obtained. The one soluble (A) and the other insoluble (B) in hot water. The soluble portion melted at 173°C. Soluble in alcohol, ether, and acetic acid. Insoluble in cold benzene. Yield = 0.12 Gm. This acid was identical with that obtained by directly chlorinating β -(4-methoxy-phenyl)-succinic acid as in method II.

Analysis:— Found Cl = 23.9 per cent. Equivalent = 147
 $C_{11}H_{10}O_5Cl_2$ Requires Cl = 24.2 „ „ „ = 146.5

Method II:—5 Gms. of β -(4-methoxy-phenyl)-succinic acid (Lapworth and Baker, J.C.S. 127, 560) were dissolved in glacial acetic acid and chlorine gas was passed through in excess, as shown by the deep yellow colour of the solution. The acetic acid was evaporated on water bath and the residue was purified by crystallization from hot water. *m.p.* 173°C. Yield 2.5 Gms.

11. 3:5-Dichloro-anisic acid (*m.p.* 200°C.):—The insoluble portion (B) mentioned in (10) on crystallization from dil. acetic acid melted at 200°C. It was identified as 3:5 diachloro-anisic acid by means of its mixed melting point with the known compound (J.C.S. 123, 1426.)

12. β -(3:5-Di-bromo-4-methoxy-phenyl)-glutaric acid (*m.p.* 211°C.):—2 Gms. of (4-methoxy-phenyl)-glutaric acid were mixed with 1 c.c. of bromine in a flask, and the reaction was moderated by cooling the mixture. It was allowed to stand for overnight and the reaction mass was boiled with water to remove soluble impurities. It was crystallized from acetic acid. *Mp.* 211°C. Soluble in ether, acetic acid and alcohol. Insoluble in water and benzene. Yield 0.9 Gm.

Analysis:— Found Br = 40.5 per cent. Equivalent = 197
 $C_{12}H_{12}O_5Br_2$ Requires Br = 40.5 „ „ „ = 198.
 Barium salt:— Found Ba = 25.1 per cent.
 $C_{12}H_{10}O_5Br_2Ba$ requires Ba = 25.7 „ „ „

13. β -(3:5 Di-bromo-4-methoxy-phenyl) - γ -butyro lactone (*m.p.* 98°C.):—It was prepared from β -(3:5-di-bromo-4-methoxy-

phenyl)-glutaric acid as in (9). On crystallization from dil. alcohol it melted at 98°C. Yield 0.62 Gm.

Analysis :— Found Br = 45.7 Per cent.

$C_{11}H_{10}O_3Br_2$ requires Br = 45.71 „ „

14. β -(3:5-Di-bromo-4-methoxy-phenyl)-succinic acid (mp. 198°C.) :—The above lactone (13) was oxidised as the corresponding chloro-compound. The crude oxidation product was purified by crystallization from hot water when two portions were obtained, one soluble (A) and the other insoluble (B) in hot water. The soluble portion melted at 198°C. This acid could also be obtained by directly brominating β -(4-methoxy-phenyl)-succinic acid as in method II.

Analysis :— Found Br = 41.82 Per cent. Equivalent = 190.1

$C_{11}H_{10}O_5Br_2$ requires Br = 41.88 „ „ „ = 191

Method II :—5 Gms. of β -(4-methoxy-phenyl)-succinic acid (J. C. S. 127, 560) were treated with 2.5 c.cs. of bromine in a dry test tube. The mixture was warmed on a water bath under a reflux condenser for half an hour, and allowed to stand overnight. The reaction product was purified by crystallization from hot water. Mp. 198°C. Soluble in alcohol, ether, and acetic acid. Insoluble in cold benzene.

15. 3:5-Di-bromo-anisic acid (m.p. 213°C.) :—During the oxidation of β -(3:5-di-bromo-4-methoxy-phenyl)- γ -butyrolactone a water insoluble product (B) was isolated along with the succinic acid. On crystallization from acetic acid it melted at 213°C. and was identified as 3:5-di-bromo-anisic acid by its mixed melting point with the known compound (Crepsi, G. 11,425).

16. Di-ethyl-2-(4'-methoxyphenyl)-4:5-diketo-pentamethylene 1:3 dicarboxylate (mp. 123°C.) :—2 Gms. of diethyl ester of β -(4-methoxy-phenyl)-glutaric acid were dissolved in 30 c.cs. of anhydrous ether; 1 Gm. of oxalic ester was added and the mixture was poured in a flask containing 0.3 Gm. of granulated-sodium dissolved. The flask was allowed to stand overnight when the sodium salt was decomposed by hydrochloric acid and extracted with ether. The ethereal layer was shaken several times with 1 to 2 c.cs. of dilute sodium hydroxide. The earlier extracts on acidification gave comparatively impure product while the later extracts immediately gave a solid, on acidification. It was further purified by crystallization from alcohol. Mp. 123°C. Yield 0.8 gram. Soluble in alcohol and ether. Insoluble in sodium bicarbonate solution. Its alcoholic solution gave a dark violet coloration with ferric chloride.

Analysis :— Found C = 62.01; H = 5.8 per cent

$C_{13}H_{20}O_7$ requires C = 62.07; H = 5.74 „ „

Similar products were obtained when this reaction was applied to β -(halogen-4-methoxy-phenyl)-glutaric acids.

The following table contains various derivatives such as anhydrides, esters, semi-anilides etc, obtained from the glutaric and succinic acids during the course of the investigation.

| Substance. | M.P. °C. | Formula. | Analysis | |
|--|--------------------|----------------------|-----------------|--------------------|
| | | | Found per cent. | Required per cent. |
| From β - (4 - Methoxy-phenyl)-glutaric acid. | | | | |
| 1. Anhydride* | 152 | $C_{12}H_{12}O_4$ | C=64.78H=5.23 | C=64.86 H=5.4 |
| 2. Semianilide | 157 | $C_{18}H_{15}O_4N$ | C=68.82H=5.9 | C=69.02 H=6.07 |
| 3. Diethylester* | B.P. 206/14m.m. | $C_{16}H_{22}O_5$ | C=65.1 H=7.39 | C=65.31 H=7.48 |
| 4. Acid-ester | 78 | $C_{14}H_{18}O_5$ | C=62.89H=6.53 | C=63.16 H=6.76 |
| 5. Phenacylester | 95 | $C_{28}H_{40}O_7$ | C=70.7 H=5.39 | C=70.9 H=5.4 |
| From β - (3-Iodo-4-anisyl)-glutaric acid. | | | | |
| 6. Anhydride | 148 | $C_{12}H_{11}O_4I$ | I=37.2 | I=37.29 |
| 7. Semianilide | 182 | $C_{13}H_{15}O_4NI$ | I=28.9 | I=28.93 |
| 8. Diethylester | 83 | $C_{16}H_{21}O_5I$ | I=30.19 | I=30.24 |
| 9. Dimethylester | 79 | $C_{14}H_{17}O_5I$ | I=32.25 | I=32.4 |
| 10. Phenacylester | 131 | $C_{28}H_{35}O_7I$ | I=20.8 | I=20.16 |
| From β - (3-Bromo-4-anisyl)-glutaric acid | | | | |
| 11. Anhydride | 143 | $C_{12}H_{11}O_4Br$ | Br=26.5 | Br=26.75 |
| 12. Semianilide | 150 | $C_{13}H_{15}O_4NBr$ | Br=20.0 | Br=20.4 |
| 13. Diethylester | 66 | $C_{16}H_{21}O_5Br$ | Br=21.3 | Br=21.45 |
| 14. Dimethylester | 74 | $C_{14}H_{17}O_5Br$ | Br=22.8 | Br=23.19 |
| 15. Phenacylester | 125 | $C_{28}H_{35}O_7Br$ | Br=14.4 | Br=14.46 |
| From β - (3-Chloro-4-anisyl)-glutaric acid | | | | |
| 16. Anhydride | 128 | $C_{12}H_{11}O_4Cl$ | Cl=13.72 | Cl=13.92 |
| 17. Semianilide | 143 | $C_{18}H_{18}O_4Cl$ | Cl= 9.9 | Cl=10.22 |
| 18. Diethylester | 40.5 | $C_{16}H_{21}O_5Cl$ | Cl=10.65 | Cl=10.8 |
| 19. Dimethylester | 59 | $C_{14}H_{17}O_5Cl$ | Cl=11.77 | Cl=11.83 |

* Already described by Jackson and Kenner, J.C.S. 1924, 1660.

Analysis

Substance M.P. °C. Formula Found per cent. Required per cent.

From β (3 : 5-Di-chloro-4-anisyl)-glutaric acid

| | | | | |
|-------------------|-------------------|------------------------|---------|----------|
| 20. Anhydride | 182 | $C_{12}H_{10}O_4Cl_2$ | Cl=24.1 | Cl=24.57 |
| 21. Semianilide | 172 | $C_{13}H_{17}O_4NCl_2$ | Cl=18.5 | Cl=18.55 |
| 22. Diethylester | B.P. 320Decomp | $C_{16}H_{20}O_6Cl_2$ | Cl=17.8 | Cl=17.84 |
| 23. Dimethylester | 63.5 | $C_{14}H_{16}O_6Cl_2$ | Cl=21.0 | Cl=21.19 |
| 24. Phenacylester | 120 | $C_{23}H_{24}O_7Cl_2$ | Cl=12.8 | Cl=13.03 |

From β -(3 : 5-Dibromo-4-anisyl)-glutaric acid.

| | | | | |
|-------------------|---------------------|------------------------|----------|----------|
| 25. Anhydride | 233 | $C_{12}H_{10}O_4Br_2$ | Br=41.9 | Br=42.3 |
| 26. Semianilide | 180 | $C_{13}H_{17}O_4NBr_2$ | Br=33.9 | Br=33.97 |
| 27. Diethylester | B. P. 315Decomp. | $C_{16}H_{20}O_6Br_2$ | Br=35.1 | Br=35.4 |
| 28. Dimethylester | 62 | $C_{14}H_{16}O_6Br_2$ | Br=37.69 | Br=37.73 |

From Diethyl 2-(R) 4 : 5-diketo-pentamethylene-1-3-dicarboxylates

| | | | | |
|----------------------------------|-----|-----------------------|----------|----------|
| 29. R=3-Chloro -4-anisyl | 126 | $C_{13}H_{19}O_7Cl$ | Cl=9.12 | Cl=9.28 |
| 30. R=3-Bromo -4-anisyl | 129 | $C_{13}H_{19}O_7Br$ | Br=18.6 | Br=18.74 |
| 31. R=3-Iodo-4 -anisyl | 133 | $C_{13}H_{19}O_7I$ | I=26.6 | I=26.8 |
| 32. R=3-5-Di- chloro-4-anisyl | 164 | $C_{13}H_{13}O_7Cl_2$ | Cl=16.93 | Cl=17.03 |
| 33. R=3-5-Di- bromo-4-anisyl | 168 | $C_{13}H_{13}O_7Br_2$ | Br=31.2 | Br=31.6 |

From 3 : 5-Dibromo-anisaldehyde

| | | | | |
|---------------------------|----------------|------------------------|---------|----------|
| 34. Semi-carbazone | 236 Decomp. | $C_9H_5O_2Br_2N_2$ | Br=47.5 | Br=47.62 |
| 35. Phenyl-hydro- zone | 135 | $C_{13}H_{10}OBr_2N_2$ | Br=43.1 | Br=43.24 |

From β - (3 : 5-Dibromo-4-anisyl)-succinic acid :—

| | | | | |
|---------------|-----|--------------------|---------|----------|
| 36. Anhydride | 110 | $C_{11}H_9O_4Br_2$ | Br=43.9 | Br=43.93 |
|---------------|-----|--------------------|---------|----------|

From β - (3 : Bromo-4-anisyl)-succinic acid :—

| | | | | |
|---------------|-----|------------------|---------|---------|
| 37. Anhydride | 168 | $C_{11}H_9O_4Br$ | Br=27.8 | Br=28.0 |
|---------------|-----|------------------|---------|---------|

Analysis

| Substance. | M.P. °C. | Formula. | Found per cent. | Required per cent. |
|------------|----------|----------|-----------------|--------------------|
|------------|----------|----------|-----------------|--------------------|

(3 - Bromo-4-anisyl)-succinic acid :—

| | | | | |
|--|-----|---------------------|----------------------|---------------------|
| 38. (3-Bromo-4-anisyl)-succinic acid | 175 | $C_{11}H_{11}O_5Br$ | Br=26.28 Equi=151 | Br=28.0 Equi=152 |
|--|-----|---------------------|----------------------|---------------------|

From (3 : 5-Dibromo-4-hydroxy)-benzaldehyde :—

| | | | | |
|-----------------------|----------------|--------------------|---------|----------|
| 39. Semi-carbazone of | 233 Decomp. | $C_8H_6O_2Br_2N_2$ | Br=49.6 | Br=49.68 |
|-----------------------|----------------|--------------------|---------|----------|

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A NOTE ON THE CONDENSATION OF ETHYLENE CHLORHYDRIN WITH RESORCINOL.

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INTRODUCTION

As a preliminary to the preparation of *2-hydroxy-4-(β -hydroxy-ethoxy)-acetophenone* which was required in an attempt to synthesise dihydrofuranflavone (Motwani and Wheeler, J. C. S., 1935, 1098), ethylene chlorhydrin was condensed with resorcinol. Two ethers have been obtained (i) *m-(β -hydroxy-ethoxy)-phenol* and (ii) *1:3 di-(β -hydroxy-ethoxy)-benzene*, of which the former is new. Rindfusz, Ginnings and Harnack (J. A. C. S., 1920, 42, 157) condensed ethylene chlorhydrin with resorcinol in presence of sodium ethylate and obtained an impure di-ether. They did not isolate the mono-ether, which contaminated the di-ether. In the present work the condensation was effected in presence of aqueous alkali. This aqueous alkali method is better, in that the completion of the reaction, in the case of insoluble ethers, is marked by the aqueous layer losing its colour, which is initially red. The di-ether has now been obtained in a pure state.

EXPERIMENTAL

m-(β hydroxy-ethoxy)-phenol. A solution of resorcinol (1 mol.; 22g) in 40% KOH (1 mol.; 28 cc.) was refluxed with ethylene chlorhydrin (1mol.; 16g.) at 100° for 3 hours. The reaction mixture was filtered from potassium chloride and extracted with ether. After removal of the ether, the extract was fractionally distilled. Three portions were collected at 2 mm. and identified.

- I b.p 160-170° about 3 g. ; resorcinol ;
- II „ 185-195° about 10g. ; *m-(β -hydroxy-ethoxy)-phenol* ;
- III „ 200-210° about 5-6g. ; mixture of II and the di-ether.

m-(β -hydroxy-ethoxy)-phenol was soluble in alkali and gave a bluish-black coloration with aqueous ferric chloride. (Found C, 62.5; H, 6.0; $C_8H_{10}O_3$ requires C, 62.3; H, 6.5 %). The *diacetyl* derivative crystallised from rectified spirit in thin plates, m. p. 75°. (Found C, 60.4; H, 6.0; $C_{12}H_{14}O_5$ requires C, 60.5; H, 5.9%). The *dibenzoyl*

derivative crystallised from dilute alcohol in microscopic needles, m. p. 90–91°. (Found C, 72.8; H, 5.2; $C_{22}H_{18}O_5$ requires C, 72.9; H, 5.0%) The ether (1 mol.) and phosphorous pentachloride (2 mols.) were refluxed at 130–135° for an hour. The oil distilled and collected at 165–170°/2 mm. was hydrolysed when *m*-(β -hydroxy-ethoxy)-chlorobenzene was obtained. It crystallised from benzene in prismatic needles, m. p. 78–79°. It is insoluble in alkali and does not give any coloration with ferric chloride. (Found Cl, 20.4; $C_8H_9O_2Cl$ requires Cl, 20.6%).

1:3-di-(β -hydroxy-ethoxy)-benzene. A solution of resorcinol (1 mol.; 22 g.) in 40% KOH (2.25 mol.; 63 cc.) was refluxed with ethylene chlorhydrin (2.25 mols.; 36 g.) at 100° for 3 hours. The thick oil which was insoluble in ether was separated from the aqueous layer and kept overnight in the refrigerator. The separated solid was filtered off, and a further quantity collected by cooling the filtrate in freezing mixture. Total yield, 18 g. It crystallised from hot water in thin pinkish needles, m.p. 95–96°. (Rindfusz and others, *loc. cit.*, give 81°). (Found C, 60.5; H, 7.1; $C_{10}H_{14}O_4$ requires C, 60.6; H, 7.1%). The *diacetyl* derivative crystallised from aqueous alcohol in prismatic needles, m. p. 75–76°. (Found C, 59.5; H, 6.5; $C_{14}H_{18}O_6$ requires C, 59.6; H, 6.4%). The *dibenzoyl* derivative crystallised from aqueous alcohol in microscopic needles, m. p. 110°. (Found C, 70.8; H, 5.6; $C_{24}H_{22}O_6$ requires C, 70.9; H, 5.4%). When the ether (1 mol.) was treated with phosphorous pentachloride (2 mols.) at 100° for an hour and the resulting oil distilled at 1 mm., *1:3 di-(β -chloro-ethoxy)-benzene* coming over at 130–150°, solidified on cooling. It crystallised from p. ether in prismatic needles, m. p. 63–64°. (Found Cl, 30.0%; $C_{10}H_{12}O_2Cl_2$ requires Cl, 30.2%).

(Received July 6, 1935)

A NEW METHOD FOR THE SYNTHESIS OF α SUBSTITUTED GLUTACONIC ACIDS.

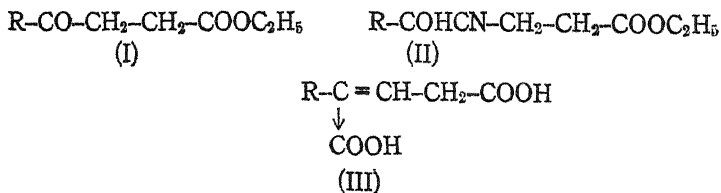
By

NAGESH LAXMAN PHALNIKAR and KRISHNA SHRINIVAS NARGUND

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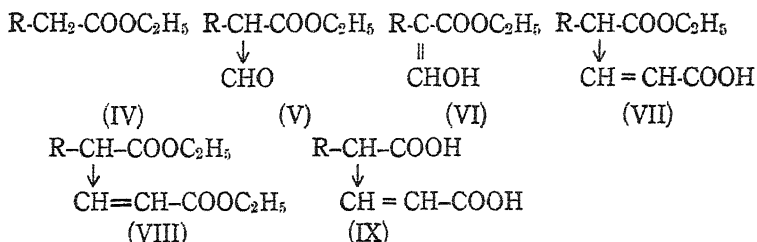
The only methods at present available for the synthesis of α substituted glutaconic acids are based on the alkylation of the parent acids. Thus Conrad and Gutzeit (Ann 188) 222 257) prepared the alkylated glutaconic acids by alkylating the yellow sodium compound which they obtained by the action of chloroform on the sodium compound of ethyl malonate. This method has been further extended by Thorpe (J.C.S. 1911 T 2191). The method, however, cannot be applied for the preparation of α phenyl glutaconic acid, because a phenyl radical cannot be introduced like an alkyl radical due to the unreactivity of the halogen substitution products of benzene. The present work was undertaken with a view to devise a general method which could be utilised for the synthesis of α phenyl glutaconic acid.

An attempt was first made to use the following reactions for this purpose. A ketonic ester (I) on treatment with hydrocyanic acid would yield a cyanohydrin (II). This on dehydration followed by hydrolysis would give the glutaconic acid (III).



This method though useful for the preparation of α methyl glutaconic acid, is, however, useless for the synthesis of α phenyl glutaconic acid because the cyanohydrin of ethyl β benzoyl propionate (II when R = C₆H₅) could not be obtained.

The following scheme represents a method by which an α substituted glutaconic acid can be prepared.



Wislicenus (Ber 20 2930) has shown that an ester having a CH_2 group next to the carbethoxyl group can be condensed with ethyl formate in presence of molecular sodium or sodium ethoxide to give a mixture of aldehydic ester (V) and a hydroxy methylene ester (VI). The aldehydic ester can then be condensed with malonic acid in presence of pyridine and piperidine yielding the acid ester of the glutaconic acid (VII). For the sake of purification it is convenient to convert the acid ester (VII) into the di-ester (VIII). This on hydrolysis gives the glutaconic acid (IX).

In practice it is not necessary to separate the compounds (V) and (VI). The condensation product containing the compounds (V) and (VI) can with advantage be used for the further synthesis.

This method has been used for the preparation of the following known glutaconic acids :

- I. α methyl glutaconic acid.
- II. α benzyl glutaconic acid.

It has been used for the preparation of the hitherto unknown α phenyl glutaconic acid. The study of the derivatives of α phenyl glutaconic acid is in progress.

It is interesting to note that the glutaconic acids obtained by this method are the trans-acids.

(Experimental)

α methyl glutaconic acid :—

A mixture of ethyl formate (37 grms.) and ethyl propionate (57 grms.) was added to molecular sodium (11.5 grms.) suspended in dry ether (500 cc.) and cooled in a freezing mixture. After ice was added the ether layer containing the unreacted substances was removed. The aqueous layer was acidified with cold dilute sulphuric acid, extracted with ether and the ethereal solution was dried over calcium chloride and the product recovered. The yield was 20 grms. This was condensed with malonic acid (16 grms.) in presence of pyridine (15 grms.) and piperidine a few drops by heating on the water bath for 5 hours. The condensation proceeded with

copious evolution of carbon dioxide. The cooled product was poured in dilute hydrochloric acid and extracted with ether. The ethereal solution was dried over calcium chloride and the product recovered. The acid ester of α methyl glutaconic acid could not be purified by vacuum distillation. Hence the above ester (17 grms.) was refluxed with absolute alcohol (70 grms.) saturated with dry hydrogen chloride. Ethyl α methyl glutaconate, [formula VIII $R = CH_3$] which is obtained in the quantitative yield, had B. P. $180-185^\circ$ at 120 m.m. Thorpe and Wood [J.C.S. 1913 T 1579] give B.P. 165° at 60 m.m. This ester on hydrolysis either by acid or by alkali yields trans α methyl glutaconic acid m.p. 144° identical with an authentic specimen of trans. α methyl glutaconic acid prepared according to the method of Thorpe and Wood [Loc. cit.].

α Benzyl glutaconic acid :—The condensation of ethyl hydrocinnmate (36 grms.), ethyl formate (15 grms.), sodium (4.6 grms.) and dry ether (400 c. c.) yielded 17 grms. of the mixture of compounds (V) and (VI) [where $R = C_6H_5-CH_2$]. This crude condensation product was condensed with malonic acid (9 grms.) in presence of pyridine (8 grms.) and a few drops of piperidine. The yield of the mono-ester of α benzyl glutaconic acid was 16 grms. It was converted into the diester in the usual way. Ethyl α benzyl glutaconate [yield 8 grms.] had B. P. 180° at 20 m. m. [Compare Bland and Thorpe J.C.S. 1912 T 886.] On acid hydrolysis this gave trans α benzyl glutaconic acid m. p. 152° , equivalent wt. 111. It was identical with the trans α benzyl glutaconic acid of Bland and Thorpe. [loc. cit.]

α Phenyl glutaconic acid :—Ethyl phenyl acetate (71 grms.) ethyl formate (38 grms.), sodium (11.5 grms.) and dry ether (400 c.c.) gave 60 grms. of the condensation product. The whole of it when treated with malonic acid (30 grms.), pyridine (25 grms.) and piperidine a few drops gave 60 grms. of the acid ester of α phenyl glutaconic acid. It was then converted into diester. Ethyl α phenyl glutaconate [formula VIII $R = C_6H_5$] had B. P. 220° at 80 m. m., density at 30° 1.0712 and refractive index at 30° 1.50923. On hydrolysis it gave α phenyl glutaconic acid m. p. 164° , equivalent wt. 103.5. The silver salt contained 51.11 per cent. of silver.

[Found: C, 64.15; H, 4.78. $C_{11}H_{10}O_4$ requires C, 64.07; H, 4.85.
Equivalent wt. = 103.0]

Our best thanks are due to the University of Bombay for a grant to one of us [K.S.N.] for research.
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C-ALKYL RESORCINOLS. I.—4 : 6-DIETHYLRESORCINOL AND ITS REACTIONS.

By

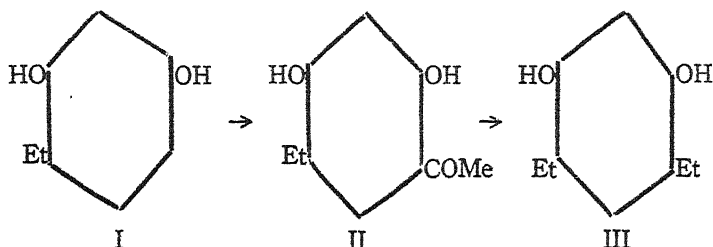
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C-alkyl resorcinols have recently attracted considerable attention for the last few years from the point of view of chemical constitution and antiseptic activity. They have also an interest of their own, as many C-alkyl resorcinol derivatives are encountered as degradation products of naturally occurring substances like lichens etc.

Samant has, in this laboratory, exhaustively studied the chemistry of 4-ethylresorcinol (Bombay University M. Sc. Thesis, 1935). In the present work, the chemical reactions of 4 : 6-diethylresorcinol which appears to have been little studied, have been investigated.

4 : 6-Diethylresorcinol (III) was synthesised from 4-ethylresorcinol (I) essentially by the method of Weiss and Kratz (Monatsch., 1929, 51, 386) as follows :—



5-ethylresorcinol-2-one (II) was prepared (i) by the Nencki reaction (Weiss and Kratz, loc. cit.), and also (ii) by the Höesch reaction. Its constitution is established by the fact that it yields, on reduction 4 : 6-diethylresorcinol, identical with the reduction product of 4 : 6-diacetylresorcinol, whose constitution has been definitely proved by Baker (J., 1934, 71).

The ketone was characterised by its phenylhydrazone, oxime, semicarbazone and the dibenzoyl derivative. Bromination in chloroform solution with 1 mol. of bromine gave a monobromo compound, 5-ethyl-2 : 4-dihydroxy-3-bromoacetophenone; with excess of bromine a tribromo derivative, 5-ethyl-3-*u-u*-tribromo-2 : 4-dihydroxy acetophenone was obtained. Clemmensen reduction of the

ketone yielded 4:6-diethylresorcinol (Klarmann, J. Amer. Chem. Soc., 1926, 48, 2358; Weiss and Kratz, loc. cit.: Rosenmund, Buchwald and Deligiannis, Arch. Pharm., 1933., 271, 342).

The phenol gave a sparingly soluble p-nitrobenzoyl derivative and afforded a monocarbomethoxy derivative on carbomethoxylation. It coupled with benzenediazonium chloride forming 2:6-dihydroxy-3:5-diethyl-azobenzene. Mercuration with mercuric acetate gave 4:6-diethyl-2-acetoxy mercury-resorcinol, while condensation with formaldehyde in acid medium afforded 2:6:2':6'-tetrahydroxy-3:5:3':5'-tetraethyl diphenyl methane. The two latter compounds are expected to be of particular interest from the point of antiseptic activity. Condensation with malic acid and acetoacetic ester by the method of Pechmann and Duisberg (Ber., 1883, 16, 2119) in the presence of 75% sulphuric acid, gave 6:8-diethyl-5-hydroxy coumarin and 4-methyl-6:8-diethyl-5-hydroxy coumarin respectively. These 5-hydroxy-coumarin derivatives are of interest as the α -pyrone ring closure takes place in position 2 in the resorcinol nucleus.

EXPERIMENTAL.

4-Ethylresorcinol. Resacetophenone prepared by the simplified method of Robinson and Shah (J., 1934, 1494) was reduced with zinc amalgam, prepared by the improved process of the same authors (loc. cit.).

5-Ethylresacetophenone. (i) By the Nencki-Sieber method:—Fused zinc chloride (50 g.) was dissolved in boiling glacial acetic acid (50 c.c.) and 4-ethyl resorcinol (33 g.) added to the cooled mixture, which was then boiled for 1-2 minutes and then allowed to cool. Dilute (1:1) hydrochloric acid (100 c.c.) was added to the cold mixture, when crystals began to separate. After a few hours the crystals were collected, and crystallised from hot benzene in rhombic plates m. p. 118-119°. Yield 35 g. Weiss and Kratz (loc. cit.) give m. p. 115° and Rosenmund, Buchwald and Deligiannis (loc. cit.) give m. p. 118-119°.

(ii) By the Höesch method:—To a solution of 4-ethylresorcinol (7 g.) and acetonitrile (3.2 g) in dry ether (40 c. c), powdered fused zinc chloride (2 g.) was added, and dry hydrogen chloride passed into the mixture, cooled by a freezing mixture. The ketimide hydrochloride began to separate after two hours, after which hydrogen chloride was passed for one hour more. After leaving overnight in the frigidaire, the ether was poured off, and the crystalline precipitate (5 g.) after washing with dry ether was crystallised from glacial acetic acid in white shining plates m. p. 245° (Found: Cl, 16.2,

$C_{10}H_{14}O_2NCl$ requires, cl, 16. 5%). The crystals were boiled with dilute (1 : 1) hydrochloric acid (100 c. c.) for 2 hours. On cooling grayish plates of the ketone separated, which were collected and crystallised from benzene in rhombic plates m. p.—and mixed m. p. with the product from (i), 118–119°.

Dibenzoyl derivative. A mixture of the ketone (1 g.), benzoyl chloride (2 g.) and pyridine (10 c.c.) was left at ordinary temperature overnight. It was then acidified with dilute sulphuric acid, and the semisolid mass was extracted with ether. The ether extract was repeatedly washed with dilute sodium hydroxide and finally with water. The oily residue from ether extract solidified after standing several days in the frigidaire. The solid 2 : 4-benzoyloxy-5-ethylacetophenone crystallised from dilute alcohol in colourless needles m. p. 91–92°. It is insoluble in alkali and does not give coloration with alcoholic ferric chloride (Found : C, 74.6 ; H, 4.8. $C_{24}H_{20}O_5$ requires C, 74.2 ; H, 5.1%).

The phenylhydrazone prepared by boiling together phenylhydrazine hydrochloride, sodium acetate and the ketone in dilute acetic acid solution for 3 hours, crystallised from dilute alcohol in yellow shining plates m.p. 232–233° (Found : N, 10.0. $C_{18}H_{13}O_2N_2$ requires, N, 10.4).

The oxime, prepared by the usual method, crystallised from benzene in colourless plates m. p. 141–143° (Found : N, 7.2. $C_{10}H_{13}O_2N$ requires N, 7.2%).

The semicarbazone was readily obtained by refluxing a mixture of the ketone, sodium acetate and semicarbazide hydrochloride for 2 hours in aqueous alcoholic solution. It is sparingly soluble in most solvents and was crystallised from boiling glacial acetic acid in yellow needles m.p. 300–302° (Found : N, 17.6. $C_{11}H_{15}O_3N_3$ requires N, 17.7%).

5-Ethyl-2 : 4-dihydroxy-3-bromo-acetophenone :—Bromine (1.6 g) in chloroform solution was added to the ketone (1 g.) dissolved in the same solvent, when fumes of hydrogen bromide were evolved. The mixture was left overnight and on evaporation of the chloroform, yellowish oily globules separated, which solidified to a yellow crystalline mass. The solid bromo compound crystallised from alcohol in pale yellow needles m.p. 123–125°. Mixed m.p. with 2 : 4-dihydroxy-5-ethylacetophenone, 91–97° (Found : Br, 30.7. $C_{10}H_{11}O_3$ Br requires Br, 30.9%). It is easily soluble in the common organic solvents.

5-Ethyl-3- ω - ω -tribromo-2 : 4-dihydroxyacetophenone :—The bromination was carried out as in the preceding case, but

excess (4 g.) of bromine was used. Evaporation of chloroform, left a crystalline, yellow solid, which on crystallisation from rectified spirit was obtained in flat yellow needles m.p. $144-145^{\circ}$. Mixed m.p. with the monobromo compound was $95-100^{\circ}$. It is much less soluble than the monobromo compound (Found: Br, 57.7. $C_{10}H_9O_3Br_3$ requires Br, 57.60 %).

4:6-Diethylresorcinol was obtained by reduction of 5-ethylresacetophenone with hydrochloric acid and zinc amalgam prepared by the improved method of Robinson and Shah (loc. cit.). It distilled as a colourless oil at $150-151^{\circ}/7$ mm., and crystallised from benzene-petroleum in colourless rhombic plates which softened at 55° , and then melted at $65^{\circ}-67^{\circ}$. Rosenmund, Buchwald and Deligiannis (loc. cit.) and Klarmann (loc. cit.) give m.p. 71° , Weiss and Kratz (loc. cit.) give m.p. $65-71^{\circ}$. It slowly turns brown and pasty on exposure to air.

Dip-nitrobenzoyl derivative was prepared by shaking together an ethereal solution of p-nitrobenzoyl chloride and a sodium hydroxide solution of the phenol. The derivative which separated in long needles was obtained by crystallisation from acetone-ethyl alcohol in needles m. p. $163-165^{\circ}$ (Found: N, 6.0. $C_{24}H_{20}O_8N_2$ requires N, 6.1 %).

Monocarbomethoxy derivative. A mixture of the phenol (2 g.) dissolved in 2N sodium hydroxide solution and methylchlorocarbonate (3.3 g.) was shaken for two hours. The semisolid mass which separated was kept on the porous plate, and the solid residue was crystallised from petroleum ether (b. p. $65-95^{\circ}$) in colourless shining flat needles m. p. $83-85^{\circ}$. It is soluble in alkali and in the common organic solvents (Found: C, 64.3; H, 7.2. $C_{12}H_{18}O_4$ requires C, 64.3; H, 7.2 %).

2:6-Dihydroxy-3:5-diethylazobenzene :—4:6-Diethylresorcinol (0.9 g.) dissolved in normal sodium hydroxide was cooled in ice, and a cooled solution of diazobenzene chloride (from 2 g. of aniline) was gradually added with constant stirring. The separated sticky solid was dissolved in hot dilute alcohol, from which it separated in chocolate coloured needles m.p. 89° . It is very soluble in the usual organic solvents (Found: N, 10.5. $C_{16}H_{18}O_2N_2$ requires N, 10.4 %).

4:6-Diethyl-2-acetoxymercuryresorcinol :—The phenol (1 g.) in alcoholic solution was added to a suspension of mercuric acetate (2 g.) in the same solvent. The mixture turned yellow and then pink and a pinkish coloured precipitate began to separate. After some hours, the precipitate was collected and crystallised from hot

glacial acetic acid in colourless shining plates. It blackens at 200° and does not melt even at 300° (Found : Hg, 46.6. $C_{12}H_{16}O_4$ Hg requires Hg, 47.0%).

Condensation with formaldehyde:—2:6-2':6'-tetrahydroxy-3:5-3':5'-tetraethyl-diphenylmethane:—Formaldehyde solution (40%; 0.5 c. c.) was added to a suspension of 4:6-diethyl-resorcinol (1 g.) in 2N hydrochloric acid (40 c. c.) and the mixture after being thoroughly shaken was left overnight. The crystalline solid which had separated was collected and crystallised from benzene petroleum ether in rectangular plates m. p. 119° (Found : C, 71.5; H, 8.3. $C_{21}H_{23}O_4$, 0.5 H_2O requires C, 71.4; H, 8.2%).

6:8-Diethyl-5-hydroxy coumarin:—Concentrated sulphuric acid (75%; 25 c. c.) was added gradually to a mixture of 4:6-diethylresorcinol (3 g.) and malic acid (2–5 g.). The mixture was left overnight and then heated on the boiling water bath for 1 hour, cooled and then poured into water. The separated solid was crystallised from rectified spirit in shining plates having a pinkish tinge m. p. $148-149^{\circ}$ (Found : C, 71.4; H, 6.4. $C_{13}H_{14}O_3$ requires C, 71.6; H, 6.4%).

4-Methyl-6:8-diethyl-5-hydroxy-coumarin:—The phenol (3 g.) and ethyl acetoacetate (2.4 g.) were mixed together and concentrated sulphuric acid (75%; 8 c. c.) was added. Much heat was developed and a deep orange viscous liquid resulted. It was allowed to stand at room temperature for 1 hour, then heated for 1 hour on the boiling water bath, and after cooling poured into ice-water (150 c.c.). The yellow precipitate was collected and after crystallisation from rectified spirit was obtained in greyish flat needles m.p. $169-170^{\circ}$ (Found : C, 72.8; H, 7.1. $C_{14}H_{16}O_3$ requires C, 72.4; H, 6.9%).

The authors are thankful to Dr. T. S. Wheeler, Principal of the Royal Institute of Science, Bombay and to Dr. M. B. Rehman, Principal of the Ismail College, Andheri for their encouragement during the progress of the work.

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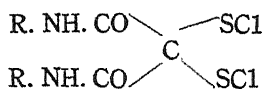
INTERACTION OF SELENIUM OXYCHLORIDE WITH THE SUBSTITUTED AMIDES OF MALONIC ACID.

BY

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Ever since the study of the nature of the hydrogens of the reactive methylene (CH_2) group situated between two negative groups was undertaken in these laboratories, efforts have been made to replace these hydrogens of the reactive methylene group by various groups and to study the effect of the adjacent radicals on such replacements. The chlorides of sulphur gave many fruitful results. Sulphur monochloride gave dithioketones and dithioethers, (Naik, J. C. S. T., 1221,, 119, 379-1166); while sulphur dichloride yielded compounds of the type



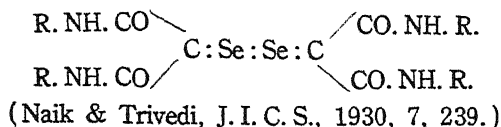
(Naik & Jadhav, J. I. C. S. 1926, 3, 260).

Reactions with Thionyl chloride also gave two types of products:

(i) Sulphoxides

and (ii) Sulphides. (Naik & Parekh, J. I. C. S. 1930, 7, 145).

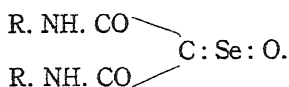
From the study of these interactions it was expected that the chlorides of selenium, being of a nature similar to that of sulphur chlorides, would also react in a similar manner. A study of the interaction of selenium tetrachloride with substances containing reactive methylene group or a substituted methylene group revealed the formation of the selenides of the type :—



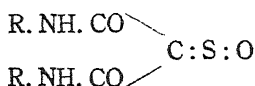
In the present study it was thought interesting to study the interactions between selenium oxychloride (SeOCl_2) and substances containing the reactive methylene group situated between two carbonyl groups. For these purposes the following substances were selected :—

- (1) Malonanilide $(\text{C}_6\text{H}_5\text{NH} \cdot \text{CO})_2\text{CH}_2$
 (2) Malon-diorthotolyl amide. $(\text{C}_7\text{H}_7\text{NH} \cdot \text{CO})_2\text{CH}_2$ -ortho.
 (2) Malon-diparatolyl amide. $(\text{C}_7\text{H}_7\text{NH} \cdot \text{CO})_2\text{CH}_2$ -para.

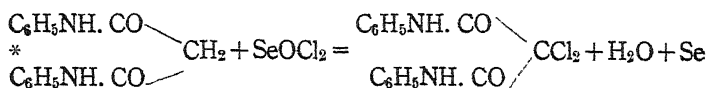
It was expected that as in the case of the interaction of these substances with thionyl chloride (Naik & Parekh, loc. cit.) this reaction would also yield the Selenoxides of the type :—



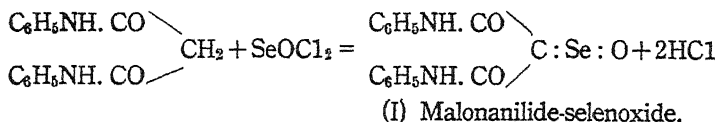
The corresponding sulphoxides obtained by Naik & Parekh (loc. cit.) were given the structure



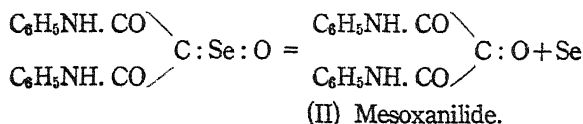
Accordingly, the reaction of selenium oxychloride with malonanilide was studied at the outset. Selenium oxychloride and malonanilide in anhydrous ether at room temperature gave dichlor-malonanilide and selenium as follows :—



In boiling anhydrous benzene the reaction proceeded in a different way and the product obtained was identified as mesoxanilide m.p. 191°C . This substance has also been obtained by J. U. Nef (J. C. S. A., 1892, 62, 1440). The interaction could be represented as taking place in two stages : At first the selenoxide is formed :

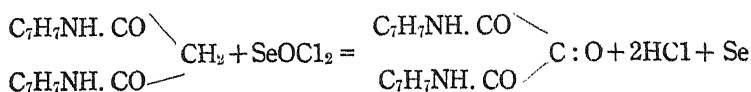


In the next stage the substance (I) seems to decompose as under :—



That the substance (I) may decompose to give rise to (II) is not surprising in view of the experimental conditions, as also in view of the fact that the selenoxide is more unstable than the corresponding sulphoxide. This is also supported by an observation viz., "...the selenium atom is far more labile than the sulphur atom in the corresponding thiocompounds." (Schmidt, Ber., 1921, 54 (B), 2067-2070).

The interaction of malondiorthotolylamide and malondiparatolylamide with selenium oxychloride followed the same course giving rise to the respective mesox-derivatives as follows:—



EXPERIMENTAL.

(i) *Interaction of malonanilide with Selenium oxychloride:*

Equimolecular quantities of selenium oxychloride and the amide were kept suspended in 50 c. cs. of anhydrous ether prepared by distilling it over sodium as well as over phosphorous pentoxide. The amide went into solution very slowly and during the interaction hydrogen chloride was found to evolve imperceptibly, after standing for 24 hours the dark red reaction mixture deposited fine silky needles. This reaction product (in the case of malonilide) was purified when fine white needles were obtained. On analysis and further identification these were revealed to be the crystals of dichloromalonanilide, m. p. 127°C . (Naik & Shah, J. I. C. S., 1927, 4, 11). The mother liquor was allowed to stand for a few days more but nothing separated out except a film of grey metallic selenium. The reaction seems to take place as represented on page (115)

It was then thought interesting to revise the experimental conditions to see if such a revision secured different results. The reaction was, accordingly, carried out in boiling anhydrous benzene solution with equimolecular quantities (Malonanilide 5gms. and selenium oxychloride 3.5 gms.) of the reactants as in the previous case. After refluxing for 24 hours a dark red solution of the reaction product was obtained. This was concentrated and was then added dropwise into a large amount of petroleum. A resinous red product was precipitated. This was isolated from the benzene-petrol mixture and was redissolved in benzene. This solution was refluxed with freshly reduced copper-gauze in order to remove the free selenium which might inhibit the crystallisation of the pure substance. The pure product was obtained after six such attempts at purification. The product was found to be a pale yellow microcrystalline powder with m. p. 191°C . Selenium as well as chlorine were found to be absent in this product. On analysis and further identification this substance was found to be mesoxanilide, (Nef, J. C. S. A., 1892, 62, 1440; Annalen, 270, 267-335). The product obtained herein combines readily with water and with alcohol to form colourless hydrate and alcohol respectively. It also combines with phenyl hydrazine in dry benzene solution. All these reactions are shown by the meso-

xanilide m. p. 190°C . obtained by Nef (loc. cit.). [Found; C, 67.06; H, 4.49; and N, 10.5; $\text{C}_{15}\text{H}_{12}\text{N}_2\text{O}_3$ requires C, 67.16; H, 4.48 and N, 10.45.]

The mixed melting points of the products as prepared by Nef's (loc. cit.) method and as prepared as described herein confirms the identity of the product obtained herein.

(II) Interaction of malondiorthotolylemide with selenium oxychloride :

The reactants were taken in equimolecular quantities as in the previous case and the reaction product was obtained in exactly the same way as described above. It was obtained after purification in the form of yellowish micro-crystalline powder melting at 172°C . [Found : C, 68.85; H, 5.5; and N, 9.5; $\text{C}_{17}\text{H}_{16}\text{N}_2\text{O}_3$ requires C, 68.9 H, 5.4 and N, 9.46.]

The substance gave a hydrate on boiling with water. This hydrate was obtained in the form of colourless needles which turned yellow at 100°C , and melted at $127\text{--}130^{\circ}\text{C}$. with decomposition. It turns blue litmus red and is soluble in dilute solution of sodium carbonate.

(III) Interaction of malondiparatolylamide with selenium oxychloride.

Mesoxdiparatolylamide was prepared in exactly the same way as the corresponding ortho derivative. The pure product melted at 187°C . [Found : C, 68.8; H, 5.35; and N, 9.55; $\text{C}_{17}\text{H}_{16}\text{N}_2\text{O}_3$ requires C, 68.9; H, 5.4 and N, 9.46.]

The product when boiled with water gives a hydrate which is obtained in the form of colourless needles melting with decomposition between $122\text{--}130^{\circ}\text{C}$. Mesoxdiparatoluidide hydrate. $\text{C}(\text{OH})_2[\text{C}(\text{OH})\text{N}(\text{C}_6\text{H}_4\text{Me})_2]_2$. Melts between $120\text{--}130^{\circ}\text{C}$, (W. R. Smith, Amer. Chem., 16. 372; 393; J. C. S. A. 1894, 66, 407).

The author takes the opportunity to thank the University of Bombay and the Government of Baroda for research grants which defrayed the expenses in connection with this investigation. He is also thankful to Dr. Naik, for extending useful help from time to time.

SYNTHETIC PRODUCTION OF CAMPHOR FROM PINENE.

PART II.

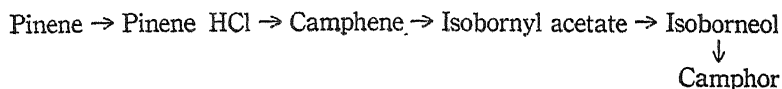
BY

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In continuation of the work described in Part I (J. Univ. Bombay, 1934, 3, Part ii, 163), we have sought to improve the yields for various stages of the synthesis, and in addition we have investigated the recovery of the reagents. The best yields and recoveries now obtained are as follows :—

PROCESS I.



| Stage. | Reagent used. | % yld. of product on reagent taken. | % yld. of product on reagent consumed. | % yld. previously reported. | Remarks. |
|--------------------|--------------------|---|--|-----------------------------|--|
| Pinene | Pinene | 80 | 80 | 80 | No recovery. |
| ↓ | | | | | |
| Pinene HCl | HCl | 75 | 75 | ... | |
| Pinene HCl | Pinene HCl | 85 | 85 | 83 | No recovery. |
| ↓ | | | | | |
| | Cresol | ... | ... | ... | 3.5 mol of cresol taken per mol of pinene HCl. 86 % of the applied cresol is recovered and reused. |
| ↓ | | | | | |
| Camphene | NaOH | 37 | 37 | | No recovery. |
| Camphene | Camphene | 82 | 82 | 80 | " |
| ↓ | | | | | |
| Isobornyl acetate. | Acetic acid. | ... | ... | ... | 250 gms. of acetic acid used per 100 gms. of camphene. 75 % of the applied acid is recovered and reused. |
| ↓ | | | | | |
| Isobornyl acetate. | Isobornyl acetate. | 85 | 85 | 80 | No recovery. |
| ↓ | | | | | |
| Isoborneol | NaOH | 34 | 34 | ... | " |
| Isoborneol | Isoborneol | 95 | 95 | 100 | " |
| ↓ | | | | | |
| Camphor | HNO ₃ | Excess of HNO ₃ originally used to act as solvent. | 84 | ... | The oxidising solution is used repeatedly. |

PROCESS II

Pinene \rightarrow Pinene hydrochloride \rightarrow Camphene \rightarrow Camphor.

(The figures are the same as in process I up to the oxidation of camphene)

| Stage | Reagent used | % Yld. of product on reagent taken. | % Yld. of product on reagent consumed. | % Yld. previously reported. | Remarks. |
|----------|---|-------------------------------------|--|-----------------------------|--------------|
| Camphene | Camphene | 50 | 63 | 50 | |
| ↓ | Acetic Acid. | ... | ... | ... | No recovery. |
| Camphor. | K ₂ Cr ₂ O ₇ | ... | ... | ... | * |
| | H ₂ SO ₄ | ... | ... | ... | * |

These results give an over-all yield of 45% for process I and 43% for Process II on pinene taken. The greatest improvement has been effected in the oxidation of camphene to camphor. Particulars of the improved methods and of the recovery of reagents are given below.

EXPERIMENTAL.

Pinene \rightarrow *Pinene hydrochloride* : (Described in Part I).

Attempts to utilise the liquid by-product are in progress.

Pinene hydrochloride \rightarrow *Camphene*.

Cresol (3.5 mols: 437 gms. of which 379 gms. is obtained by recovery from a previous preparation), and caustic soda (2.3 mols: 106 gms.) are distilled up to 150°C to remove the water formed. The aqueous distillate contains 55 gms. of cresol, which is separated and used again. Pinene hydrochloride (1 mol: 200 gms.), is added to the residue and the mixture refluxed for 4-5 hours and distilled (oil-bath). The fraction up to 160° is mostly camphene (134 gms.) and is washed with aqueous caustic soda (300 gms. of 5 % NaOH) to free it from cresol, and then with water. The solid camphene thus obtained is used without further purification. Cresol (220 gms.) comes over from 160° to dryness and is used again. The solid residue is treated with dilute sulphuric acid (1000 cc. of 10 % acid) and the cresol separated (104 gms.) is used again. The total recovery of cresol is 379 gms. (86 %) and the yield of camphene is 85 % of the theoretical. The yield is 79 % on the first run, but rises in subsequent runs as the reused cresol contains camphene.

(* 3.9 mols. of sulphuric acid and 0.8 mol. of potassium dichromate are taken per mol. of camphene. They are recovered as chrome alum in 70% yield calculated on the K₂Cr₂O₇, and 58% on the H₂SO₄ taken.)

With potassium phenoxide, a 95 % yield of camphene can be obtained with 82 % recovery of phenol, but the high price of potassium hydroxide renders it unsuitable for commercial use. This gives an over-all yield of 50 % for Process I and 48 % for Process II from pinene to camphor.

A slight increase in the yield of camphene (2-3 %) is obtained by carrying out all the distillations under reduced pressure and conducting the reaction in an atmosphere of nitrogen.

Camphene \rightarrow *Isobornyl acetate* :—

Camphene (100 gms.) and glacial acetic acid (250 gms.), are heated together at 45-55° for 2½ hours with a catalyst such as 50% sulphuric acid (20 gms.). Anhydrous sodium acetate (18 gms.) is then added to the reddish-coloured liquid to remove sulphuric acid, which otherwise causes decomposition during the recovery of acetic acid by distillation. Acetic acid (187.5 gms.) is distilled off (oil-bath) up to 130-35° and is used again. The residual ester (118 gms.) is washed with aqueous sodium carbonate and with water and is used without further purification. The final yield of ester is 82 % of the theoretical.

Isobornyl acetate \rightarrow *Isoborneol*.

Isobornyl acetate (1 mol: 100 gms.) and 80 % aqueous caustic soda (2.5 mols: 50 gms.), are refluxed at 135-145° for 6 to 8 hours. The resulting solid isoborneol (66.5 gms.) is washed free from caustic soda. The yield is 85 % of the theoretical on the ester taken.

Isoborneol \rightarrow *Camphor* :—

Isoborneol is dissolved in a mixture of five times its weight of nitric acid (35%) and one-third its weight of sulphuric acid (50%) and the solution is heated on the water bath at 75-85° for 8-10 hrs. with frequent shaking. The resulting mixture forms two layers. The upper brown layer of camphor is separated and treated with a large volume of water when camphor is precipitated and is dried and sublimed. The yield of camphor is 95% of the theoretical. Excess of nitric acid is used at the outset to act as a solvent for the isoborneol; for subsequent oxidations, the lower layer is used with addition of 70% nitric acid (66 gms. for 100 gms. of isoborneol). The yield remains constant. 25 successive oxidations were conducted using repeatedly the lower layer without any fall in the yield.

Camphene \rightarrow *Camphor* :—

Camphene (1 part: 50 gms.), is dissolved in glacial acetic acid (2 parts: 100 gms.), and potassium dichromate (1.75 parts: 87.5 gms.) and sulphuric acid (2.8 parts: 140 gms.), in water (15 parts:

750 gms.) are added, and the mixture refluxed at $115-120^{\circ}$ (oil bath) for 35–45 hrs. until it becomes green and the crude floating product when sampled has m.p. above 140° . The resulting floating camphor is filtered off and washed with 5% caustic soda solution (150–200 gms. : 7.5–10 gms. NaOH) and with water. The crude product 40 gms. is subjected to fractional sublimation twice up to 110° . The sublimed camphor weighs 28 gms. ($170-172^{\circ}$) and the residue (10 gms.) of unsublimed material is mostly camphene and can be added to 40 gms. of camphene to make up the next batch of 50 gms. Accordingly 40 gms. of camphene gives 28gms. of camphor, corresponding to a yield of 63% of the theoretical.

The filtrate is concentrated on the water bath until crystals begin to separate and it is then cooled. Chrome alum crystals separate in 70% yield on the potassium dichromate and 58% on the sulphuric acid taken.

The quantities of materials required for the preparation of 100 gms. of camphor by the two processes are as follows :—

PROCESS I.

| Materials used | Taken | Consumed. | Recovered. |
|--------------------------------|-------|-----------|------------|
| Pinene | 200 | 200 | |
| CaCl ₂ | 4 | 4 | |
| HCl | 56 | 56 | |
| Cresol | 437 | 58 | 379 |
| NaOH | 200 | 200 | |
| Acetic acid | 335 | 84 | 251 |
| CH ₃ COONa | 24 | 24 | |
| H ₂ SO ₄ | 130 | 110 | 17 |
| HNO ₃ | 49 | 49 | |

PROCESS II.

| | | | |
|---|-----|-----|--|
| Pinene | 208 | 208 | |
| CaCl ₂ | 4 | 4 | |
| HCl | 58 | 58 | |
| Cresol | 453 | 63 | 390 |
| NaOH | 150 | 150 | |
| Acetic Acid | 284 | 284 | |
| H ₂ SO ₄ | 457 | 457 | } 587gms. chrome alum recovered. |
| K ₂ Cr ₂ O ₇ | 248 | 248 | |

CONCLUSION

As a result of this further work the over-all yield of pinene to camphor in process I has been raised from 42 to 45% and in process II from 33 to 43%. In the oxidation of camphene to camphor, a reaction first achieved in this research (Part I, *loc. cit.*) the yield has been increased from 50% to 63%.

The main difficulty in carrying out the process on an industrial scale now lies in the fact that Indian turpentine is unsuitable and that imported turpentine must be used. Even with the imported turpentine the yields now obtained show a possibility of economic production, and if in process II the use of acetic acid as an addition to the reaction mixture in the oxidation of camphene to camphor could be avoided the economic prospects of the production will be good.

* [It has now been found possible to avoid the use of acetic acid. The modified process is as follows: Camphene (50 gms.), $K_2Cr_2O_7$ (80 gms.), H_2SO_4 (75 gms.) and water 500 gms. are refluxed at $115-120^\circ$ (oil-bath) as before. In the first six hours 75 gms. of H_2SO_4 in 250 cc. of water is slowly added, the mixture being shaken at intervals so that the sublimed material is returned to the reaction mixture. The melting point of the final product is 1 to 2° lower than before. The yield is unchanged.]

Our best thanks are due to the University of Bombay for a grant to one of us (B. G. S. A.) towards the expenses of the chemicals.

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* Note added in proof.

VISCOSITY MEASUREMENTS DURING THE COAGULATION OF TITANIUM DIOXIDE SOL BY MIXTURES OF ELECTROLYTES AND NON-ELECTROLYTES

By

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Literature abounds in data on the effect of non-electrolytes on the effective concentration of the coagulating electrolyte. But very few measurements have been made on the influence of non-electrolytes on the velocity of the coagulation caused by electrolytes. Most of the available data gives flocculation values. (vide. Freundlich, *Kapillarchemie* p. 463). The authors have emphasised in a previous communication (J. Ind. Chem. Soc., 1935, 12,552) that viscosity is a property which is very sensitive to changes in a colloidal system and that it has been utilised for the study of (i) the rate of coagulation and (ii) the degree of hydration of the colloid particles.

Ostwald (Trans. Farad. Soc., 1913, 9, 34) was perhaps the first to have recognised that additions of both electrolytes and non-electrolytes may raise or depress viscosity in the most varied manner. Rona and György (Biochem. Z., 1920, 105, 133) while studying the sedimentation of kaolin came to the conclusion that the velocity of sedimentation was markedly increased by the addition of non-electrolytes. Klosky (J. Phys. Chem., 1929, 33, 621) determined the relative viscosity of a silver sol containing different amounts of ethyl alcohol and found that it increases at first and then diminishes with an increase in the amount of alcohol. He also found that the precipitation values for the colloid are lowered by the addition of alcohol but that the calculated value of the boundary potential rises after the addition of twenty-five per cent. alcohol. Dhar (J. Ind. Chem. Soc., 1929, 6, 641) measured the viscosity of certain sols of metallic hydroxides and found that the viscosity decreases when peptising electrolytes are added. Bhatnagar and Bahl (Kolloid. Z., 1930, 50, 48) studied the effects of acetone, cane sugar and alcohol on the relative viscosity of an emulsion of olive oil and found an increase in viscosity: they concluded from the results of their experiments that the increased sensitiveness of the emulsion towards electrolytes is related to the lowering of the dielectric constant,

Prasad, Mehta and Desai (*J. Phys. Chem.*, 1932, 36, 1391) examined the effect of methyl, ethyl and propyl alcohols on the changes in viscosity of silicic acid gel-forming mixtures with time and explained the accelerating influence of these alcohols on the rate of increase of viscosity on the assumption of the diminution of the dielectric constant of the mixture. They, however, did not explain the retarding influence of alcohols in the acidic mixtures.

It would thus appear that the influence of mixtures of electrolytes and non-electrolytes on the changes in viscosity of a sol with time has been studied only in a few cases. Moreover, the combined effect of non-electrolytes and of the purity and concentration of a sol on the changes in viscosity with time has not been studied. The present investigation deals with the influence of methyl, ethyl and propyl alcohols on the changes in viscosity with time of titanium dioxide sol dialysed and diluted to different extent when the chlorides of potassium, magnesium and aluminium are added to it.

EXPERIMENTAL

Scarpa's apparatus (*Gazetta*, 1910, 40, 271) modified by Farrow (*J. C. S.*, 1912, 101, 347) and improved upon by Prasad, Mehta and Desai (*J. Phys. Chem.*, 1932, 36, 1384) was used for the measurement of viscosity. The apparatus (fig. 1) consists of a glass vessel A having a ground glass stopper B through which two glass tubes M and N are sealed. The tube N, sealed at one end of the viscometer bulb D and the capillary tube E, is connected at the other end, to the aspirator H through the guard tube G. Glass wool soaked in a dilute solution of sodium hydroxide is placed in the guard tubes F and G to prevent carbon dioxide and dust reaching the colloid and also to avoid any change in the concentration due to evaporation. The viscometer is connected to or disconnected from the atmosphere when necessary by turning the stoppers Q and R. On opening Q the viscometer is opened to the atmosphere while R disconnects the guard tube G from the aspirator.

After the colloidal solution is put in the viscometer suction is applied to it through the aspirator. The suction produced is proportional to the difference of level of water in the aspirator H and the bottle I, both of which are identical in capacity and are connected to each other by means of a siphon arrangement K. Another siphon arrangement L connects the bottle I to the sink. It is so adjusted that within the same time, double the volume of water flowing out of H into I flows out of I into the sink. This arrangement overcomes the difficulty of pouring in or withdrawing water to ensure constant pressure, indicated by the manometer J connected to H.

The viscometer along with the guard tube F was enclosed in an electrically heated thermostat maintained at $33^{\circ}\text{C} \pm 0.02^{\circ}$. The following were the dimensions of the viscometer used:

1. Volume of the bulb between the two fixed marks..1.3838 c.cs.
2. Diameter of the capillary.....0.1095 cm.
3. Length of the capillary.....0.6566 cm.

Five c.cs. of the sol were taken in a test tube for coagulation and in another the required amount of the electrolyte+1 c. c. alcohol diluted to five c. cs. by the addition of distilled water. The total volume of the sol+electrolyte+alcohol+water was ten c.cs. in all the experiments. This coagulating mixture was introduced into the viscometer and suction applied at 15 cms. water which was kept constant throughout the investigation. When the mixture reached the lower mark a stop watch was started and the time of rise t_1 from the lower to the upper mark was noted. The viscometer was then connected to the atmosphere and the mixture allowed to fall under its own weight: the time of fall t_2 was also noted. While mixing the sol with the alcohol and the electrolyte a second stop watch was started from which the time at which the coagulating mixture was allowed to rise and that at which it was allowed to fall in the viscometer was obtained. The mean of these times gave the interval during which the viscosity reading was taken.

The viscosity of the sol was calculated from the formula $\eta = K \left(\frac{t_1 t_2}{t_1 + t_2} \right)$ where K is a constant which was determined by finding out $\frac{t_1 t_2}{t_1 + t_2}$ for pure water whose absolute coefficient of viscosity at 33°C is known and was found to be 0.001136. The accuracy of the determination with the apparatus was tested by finding the viscosity of pure recrystallised benzene.

The sol was prepared by precipitating titanium hydroxide by adding NH_4OH to titanium tetrachloride. The precipitate was washed with hot water till free from ammonia. It was suspended in a large volume of water and boiled. At intervals, 2 N HCl was added to peptise the sol. By replacing the evaporated water from time to time, the volume of the sol was kept constant. The sol was dialysed in a parchment bag which was previously washed with hot distilled water. No titanium was detected in the dialysate during dialysis.

Twenty five c.cs. of the sol were taken, and a concentrated solution of NH_4Cl was added in excess to coagulate it. The sol was heated on a water bath at 70°C to hasten coagulation. The precipitate was washed till free from chloride. It was dried,

ignited in a silica crucible and weighed as TiO_2 . The amount of colloidal TiO_2 was found to be 2.012 grams per litre.

The electrolytes employed were the chlorides of potassium, magnesium and aluminium. Their concentrations were so selected that the time required for coagulation was about an hour except in the case of purer samples. The same concentration of the electrolytes was used in the case of the diluted sols. The non-electrolytes used were methyl, ethyl and propyl alcohols. The alcohols were kept over calcium metal, refluxed and distilled.

The original sol is designated A and the half and quarter diluted ones A/2 and A/4 respectively. All the results are not given: only a few selected ones are represented graphically in figures 2-6.

DISCUSSION.

It will be seen from the curves in figs. 2-6 that the viscosity of titanium dioxide sol to which a mixture of an electrolyte and non-electrolyte is added increases with time just as it does in the presence of electrolytes alone (cf. J. Ind. Chem. Soc., 1935, 12,552). This increase in viscosity with time is readily explained on the increased hydration of the colloid particles due to neutralization of their charge or on the supposition that it is due to the increase in size of the particles as a result of progressive coagulation.

It is to be noted, however, that the curves in figs. 2-6 are not continuous in the case of samples of the sol dialysed only for a few days. (cf. Joshi and co-workers, J. Ind. Chem. Soc., 1933, 10, 329; *ibid.*, p. 599; 1934, 11, 133). The change in the periodic nature of the curves with progress of dialysis and with dilution is given in tables 1-3 in which P, P₁, P₂ and P₃ represent diminishing periodicity and N denotes its absence.

TABLE 1
Electrolyte KCl

| Number of days for which the sol was dialysed | CH ₃ OH | | | C ₂ H ₅ OH | | | C ₃ H ₇ OH | | |
|---|--------------------|----------------|----------------|----------------------------------|----------------|----------------|----------------------------------|----------------|----------------|
| | A | $\frac{A}{2}$ | $\frac{A}{4}$ | A | $\frac{A}{2}$ | $\frac{A}{4}$ | A | $\frac{A}{2}$ | $\frac{A}{4}$ |
| 0 | P | P | P | P | P | P | P | P | P ₁ |
| 3 | P | P | P | P | P | P | P | P | P ₁ |
| 6 | P | P ₁ | P ₂ | P | P ₁ | P ₂ | P ₁ | P ₂ | P ₃ |
| 9 | P | P ₂ | P ₂ | P | P ₂ | P ₃ | P ₂ | P ₂ | P ₃ |
| 12 | P | P ₂ | P ₃ | P ₂ | P ₃ | P ₃ | P ₃ | N | N |
| 20 | N | N | ... | N | N | ... | N | N | ... |
| 25 | N | ... | ... | N | ... | ... | N | ... | ... |

TABLE 2.
Electrolyte MgCl_2

| Number of days for which the sol was dialysed | CH_3OH | | | $\text{C}_2\text{H}_5\text{OH}$ | | | $\text{C}_3\text{H}_7\text{OH}$ | | |
|---|------------------------|---------------|---------------|---------------------------------|---------------|---------------|---------------------------------|---------------|---------------|
| | A | $\frac{A}{2}$ | $\frac{A}{4}$ | A | $\frac{A}{2}$ | $\frac{A}{4}$ | A | $\frac{A}{2}$ | $\frac{A}{4}$ |
| 0 | P | P | P | P | P | P_2 | P | P | P_2 |
| 3 | P | P | P | P | P | P_1 | P | P_1 | P_2 |
| 6 | P | P | P_2 | P | P_1 | P_2 | P_3 | P_3 | N |
| 9 | P_2 | P_2 | P_3 | P_3 | P_3 | P_3 | P_3 | P_3 | N |
| 12 | P_2 | P_2 | P_3 | P_3 | N | N | N | N | N |
| 20 | N | N | ... | N | N | ... | N | N | ... |
| 25 | N | ... | ... | N | ... | ... | N | ... | ... |

TABLE 3
Electrolyte AlCl_3

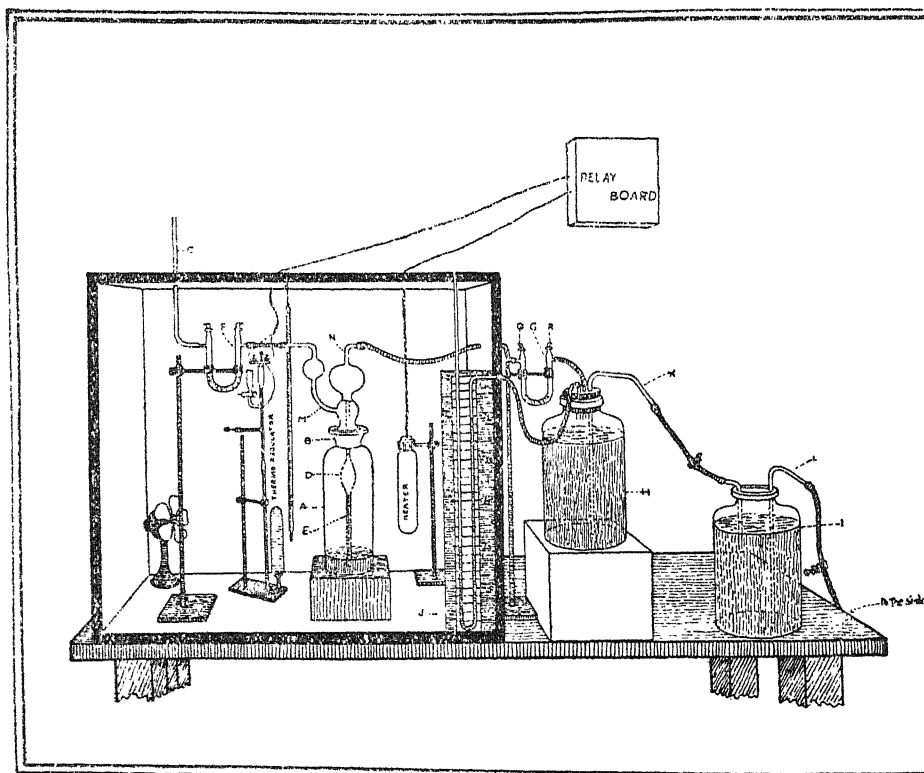
| Number of days for which the sol was dialysed | CH_3OH | | | $\text{C}_2\text{H}_5\text{OH}$ | | | $\text{C}_3\text{H}_7\text{OH}$ | | |
|---|------------------------|---------------|---------------|---------------------------------|---------------|---------------|---------------------------------|---------------|---------------|
| | A | $\frac{A}{2}$ | $\frac{A}{4}$ | A | $\frac{A}{2}$ | $\frac{A}{4}$ | A | $\frac{A}{2}$ | $\frac{A}{4}$ |
| 3 | P | P_2 | P_3 | P | P_2 | P_3 | P_1 | P_3 | P_3 |
| 6 | P | P_2 | P_3 | P_3 | P_3 | N | N | N | N |
| 9 | P_2 | P_3 | P_3 | P_3 | P_3 | N | N | N | N |
| 15 | N | N | N | N | N | N | N | N | N |
| 20 | N | ... | ... | N | N | ... | N | ... | ... |
| 25 | N | ... | ... | N | ... | ... | N | ... | ... |

It would appear from the above that the purity of the sol plays an important part in conditioning the periodic nature of the viscosity time curves—a conclusion which is in accord with the observations made in the case of coagulation of titanium di-oxide sol by electrolytes alone. Since the concentrations of the coagulating electrolytes were so chosen that complete coagulation took place in about an hour except in the case of purer samples of the sol it is obvious that the curves are periodic in nature only in the slow region of coagulation. It is to be observed that the periodic nature of the curves tends to disappear as the sol gets purer and therefore with a very pure sample of the sol it is not possible to realize experimentally the discontinuous change in viscosity with time.

On a comparison of the viscosity time curves obtained in the presence of non-electrolytes with those in their absence it will be seen that the viscosity of various samples increases by the addition of the

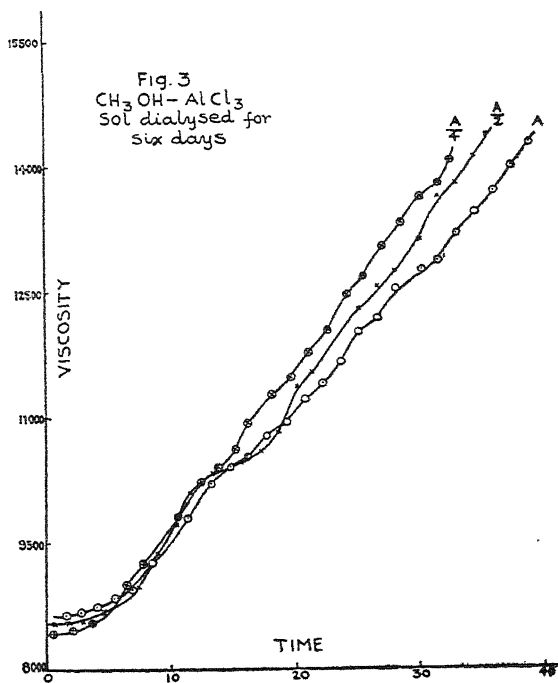
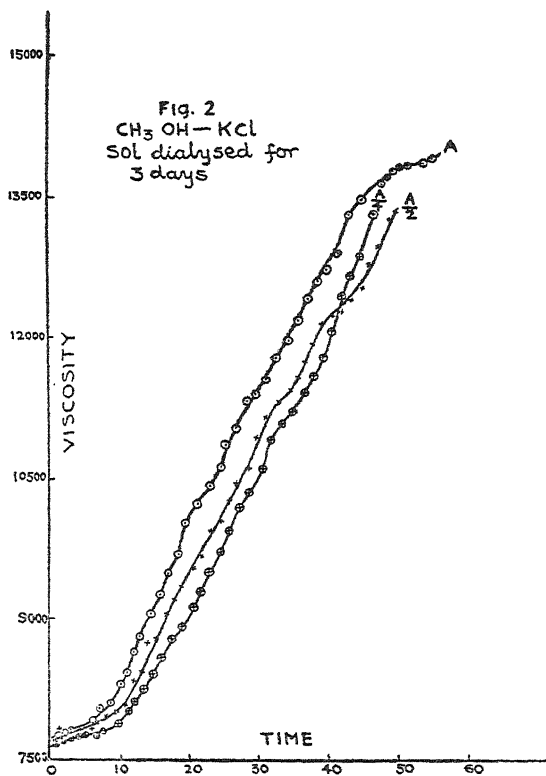
alcohols. This observation seems to be in agreement with the view that the addition of alcohols to a colloidal solution diminishes the dielectric constant of the medium with a consequent decrease in density of charge on the particles and an increase in their hydration. (cf. Freundlich, *Kapillarchemie* 1922, 637; Dhar, *J. Phys. Chem.* 1926, 30, 1646). It is also found that the rate of coagulation is greater in the presence of electrolytes+non-electrolytes than in the presence of electrolytes alone. This shows that not only an initial change takes place in the condition of the colloid particles on the addition of non-electrolytes but even subsequently either the rate of aggregation of the particles or their rate of hydration or both increase.

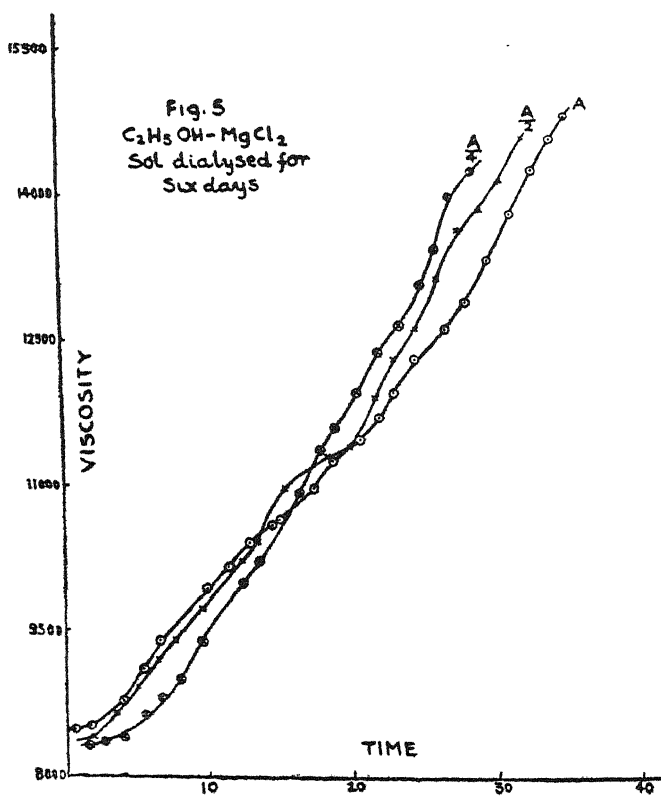
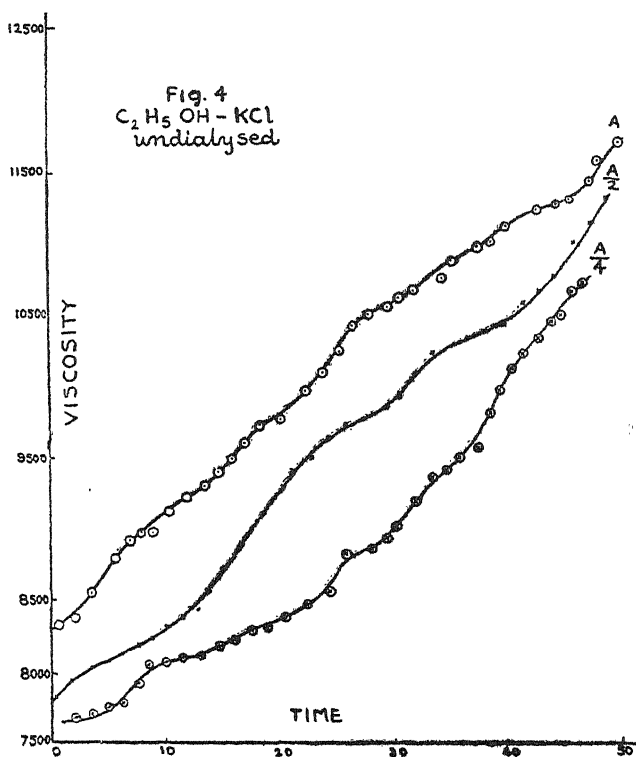
The authors are thankful to Dr. Mata Prasad for useful suggestions and help.

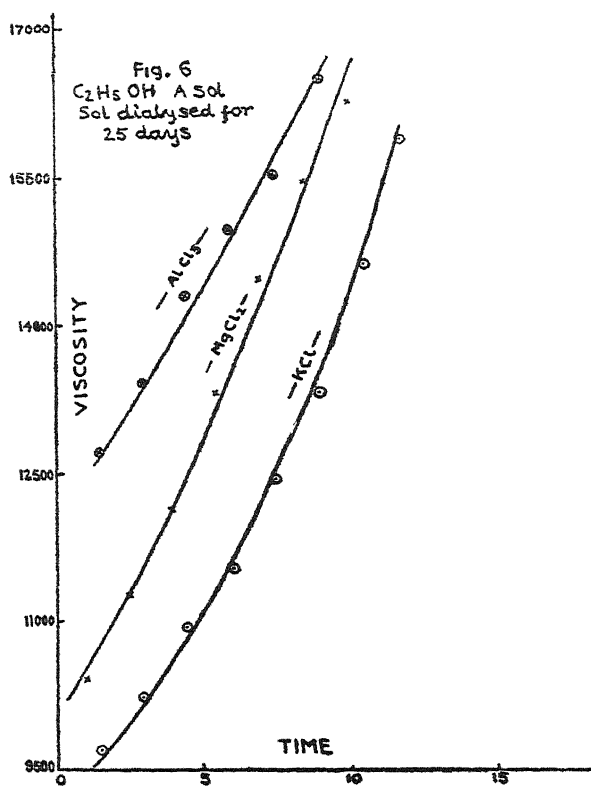


(Figure 1)

Transaction No. 16; Viscosity measurements during the coagulation of titanium dioxide sol by mixtures of electrolytes and non-electrolytes by Miss. Olive Joseph and Mr. S. M. Mehta.







THE METHODS OF MEASURING SURFACE TENSION

BY

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Several phenomena which a liquid surface exhibits form the basis of different methods employed for the determination of surface tension. Adam (Physics and Chemistry of Surfaces 1931) has classified these methods into (1) static and (2) dynamic. Fergusson (Science Progress, 9, 428, 1915) classified them into two divisions: (1) those which depend upon and (2) those which are independent of contact angle. In what follows, these methods have been reviewed in brief and the main theoretical and experimental difficulties involved in using them for determining the surface tension of liquids have been pointed out. A method developed by Fergusson (Proc. Phys. Soc., 44, 511, 1932) and improved upon by the authors is described in this paper and the results obtained for standard liquids have been compared with those obtained by previous workers.

Conditions which should necessarily be fulfilled by any method which can be used for the correct determination of surface tension are: (1) it must give results of a high degree of accuracy in a reasonable time; (2) it must be amenable to a perfect and easy temperature control and (3) it should be unimpeachable in its mathematical details.

Of the two types of methods mentioned by Fergusson, the capillary rise method is the most important of those which depend upon the contact angle. The formula deduced for the calculation of the surface tension by this method involves the height 'h', to which a liquid rises in a capillary tube of uniform bore "r", the density of the liquid 'd' and the contact angle 'θ'. It is thus essential in this method that capillary tubes of uniform bore should be used. Now it is not only difficult to have capillary tubes of uniform bore but different results are obtained when tubes of different diameters are used. However, Sugden (J. C. S., 1483 1921,) has constructed a table by means of which the best observations made by this method with tubes of any diameter can be corrected. Further, the variation in the height of the liquid column in a capillary tube due to a change in the surface tension of a liquid with temperature cannot be accurately ascertained, because the expansion of the liquid and the lowering of

the surface tension due to increase in temperature act in opposite directions. Also the contact angle is assumed to be zero or almost zero when a liquid 'wets the glass'—a term which is not correctly defined and is not clearly understood. There are other defects in this method, such as the difficulty in the cleaning and drying of the narrow capillary tube, controlling temperature etc.

Methods which do not depend upon contact angle have been divided by Fergusson (*loc. cit.*) into four different groups: (1) vibration methods, (2) the balance method, (3) methods depending on bubbles and drops and (4) the capillary tube method. The different methods belonging to each of these groups, have been discussed by him in sufficient details. Below are mentioned only the salient points regarding the above-named methods and of others which have later come into use.

Methods which depend upon the oscillation of drops and jets (cf. Rayleigh: *Proc. Roy. Soc.*, 29, 71, 1879; Bohr: *Phil. Trans.*, A, 209, 281, 1901; and Stocker: *Z. physikal. chem.*, 94, 149, 1920) and on the formation of ripples on the surface of liquids are fairly complex. They involve the measurement of the period of oscillation of small falling drops about their equilibrium figures, the measurement of the wave-length of the waves formed on the surface of jets of liquids and of ripples generated on liquid surfaces. Lord Rayleigh's theory of the former method has been supplemented by various correction factors by Bohr (*loc. cit.*) who has also devised an experimental technique which satisfies the theoretical assumptions. If all the measurements involved in these methods are not made with extreme care, the results obtained will be erroneous.

The second group of Fergusson's classification includes methods which involve the measurement of (i) the pull required to detach a ring from the surface of a liquid and (ii) the tension in a film of a liquid formed on a light frame. The accuracy of the former method depends upon the dimensions of the ring and on the thickness of the wire of which it is made. But the formulæ used for calculating the surface tension are only approximate and the results obtained are in error. Du Nöuy (*J. Gen. Physiol.*, 1, 521, 1919) has designed a convenient form of an apparatus depending upon the above mentioned principles but this yields results which are only reliable within one per cent. provided a fairly large number of precautions are taken. The second method is based on the same principles as the former, but its application is very restricted as many liquids do not form permanently stable films.

The bubble and drop methods require the measurement of excess of pressure in a hanging drop or a bubble or in a drop formed

on or underneath a glass plate and the radius of curvature of the drop or of the bubble. These methods may give results of sufficient accuracy under suitable conditions but it is not easy to measure the radius of the drop or of the bubble with great exactness. Further in the case of bubbles formed on a plate the equation correlating the surface tension of the liquid with the measurements which can be made on the bubbles is not correctly known.

The method due to Jaeger (Z. Anorg. Chem., 101, 1, 1917) is the most important of those included in the capillary tube methods. It is based on the measurement of the pressure required to release a bubble from the end of a capillary tube dipping vertically in a liquid. The formula deduced for the method is based on statical principles which require that the rate of bubbling should be exceedingly slow. Further it is essential to determine the depth of the lower end of the capillary below the surface of the outside liquid which should be contained in a fairly wide vessel.

These complications are avoided in a simple apparatus devised by Sugden (J. C. S., 125, 27, 1924) by means of which very accurate results can be obtained fairly rapidly with small volumes of liquids.

The drop-weight method (J. A. C. S. 30, 1908) which has also been used for surface tension determination is based on Tate's (Phil. Mag., 27, 176, 1864) suggestion that the weight of a drop is proportional to the radius of the tube from which it falls. However, in practice, not the whole drop, but only a part of it is collected, the rest remains sticking to the tube. This has been demonstrated by Guye and Parrot (Arch. Sc. Phys. Nat. 15, 178, 1903) from a cinematographic study of a falling drop. Harkins and Brown (J. A. C. S., 41, 499, 1919) have attempted to fill up the gap between the theory and practice of this method by laborious standardisations and by the use of correction tables but their improvements are negated because of the doubtful assumption that the fraction of a falling drop of similar shape is the same for all liquids, and that the surface tension of the standard liquid determined by one or the other methods is correct.

In all the methods excepting Sugden's described so far a fairly large amount of a liquid is required for the surface tension determination. Kipplinger (J. A. C. S., 42 472, 1920) devised a method in which only a small amount of the liquid is needed. A thread of a liquid in a capillary tube open at both ends is inclined till the meniscus at its lower end is plane. The surface tension is calculated from the formulæ.

$$T = \frac{rdl \cos \alpha}{2}$$

where α is the inclination of the capillary to the vertical.

Fergusson (Proc. Phys. Soc., 36, 1923) has developed a method in which quantities of liquids required are much smaller than those in Kipplinger's method. The method depends upon measuring the pressure which will bring the meniscus of a liquid at the lower end of a vertical capillary in a plane position. The surface tension calculations involve a knowledge of the densities of the liquids used in the capillary and that used in the manometer. The determination of the density of the liquid is impossible if the available quantity of the liquid is very small. Fergusson (Proc. Phys. Soc., 44, 511, 1932) later found that if the capillary is placed in the horizontal position and be of a diameter less than one millimeter, then density measurements are no longer required. The surface tension is given by

$$T = \frac{1}{2} h d r g$$

where h and d refer to the manometric liquid and r is the radius of the end of the capillary.

The pressure on the inner side of the thread of liquid in the capillary is increased by forcing air by means of an aspirator which can be raised to any desired position by rack and pinion screw. This arrangement gives jerks to the entire apparatus and the plane position of the meniscus does not remain steady for sufficient time. Also the capillary tube has to be fused to the manometer tube for each observation. This involves a considerable waste of time particularly when a large number of observations are to be taken. Further the results are erroneous because the manometer is not kept at a constant temperature due to which the density of the manometer liquid changes. If the method is employed for determining the surface tension of solutions, the cross-section of the capillary bore being small, the heating effect of the rays of light focussed for observing the plane position of meniscus will increase the concentration of the solution at the surface. These defects in Fergusson's method have been removed by the following alterations:—

(1) The two vessels used for adjusting the pressure have been substituted by a simple mechanical device.

(2) The capillary tube has been kept in an air-thermostat and the manometer in a water bath kept at a constant temperature. The accuracy of the results is further increased by the use of xylene (sp. gr. 0.8576) as a manometric liquid.

(3) The capillary tube has been connected to the tube leading to the manometer by means of an air-tight ground glass joint.

(4) A large flask containing water at constant temperature has been interposed in the path of the beam of light illuminating the end of the capillary.

Description of the apparatus

The apparatus used is shown in Fig. 1. It mainly consists of a horizontal capillary tube C, which is connected by a ground glass joint (fig. 1a), to the tube leading to the manometer M. The portion of the tube from C to K which is sufficiently long, is kept in an air thermostat maintained at a constant temperature. E (Fig. 1a) is a round bottomed flask containing the solution under investigation and fitting loosely to the tube C. A bulb D is fused to the tube from the manometer, through a capillary PQ and is connected by a pressure tubing to a mercury reservoir H capable of being raised or lowered by a mechanical arrangement of worm and worm wheels. B-B are water baths maintained at 30°C., the temperature at which the density of the manometric liquid was determined.

METHOD

The capillary tube was about 5 cms. long and the mean value of the diameter of its bore determined from twenty different measurements was found to be 0.0545 cm.

The capillary tube was first cleaned by means of hot chromic acid, sodium hydroxide solution and distilled water and was finally dried in a current of hot air. Approximately one cm. length of the solution was taken in the capillary which was afterwards attached to K through the ground glass joint. The atmosphere in the air thermostat was kept saturated with water vapour to prevent evaporation from the surface of the solution in the capillary tube by means of four evaporating dishes containing the same solution as under investigation.

The end of the capillary was illuminated by a milky electric bulb focussed on it by a lens. In the path of light was interposed a flask containing water maintained at constant temperature. The illuminated end of the capillary tube was focussed in the field of a long focus microscope. While viewing the bore of the capillary, which appeared as a dark circle through the microscope, the handle A was gradually turned, so as to change the pressure on the meniscus. When the pressure attains a certain value, a tiny bright spot (fig. 1b, i) appears in the dark circle in the field of view, which gradually increases in size (fig 1b ii) as the pressure increases. Finally at a critical pressure the meniscus becomes perfectly plane and the whole of the initial dark circle becomes illuminated (fig. 1b, iii). Further increase in pressure results in the diminution of this white circle due to formation of convex surface (fig. 1b, iv, v). The condition of the complete illumination of the initial dark circle in the field of view indicating plane surface of the meniscus was extremely critical as the slightest variation in the pressure at once indicated a change in the surface. Also the pressure required for this condition

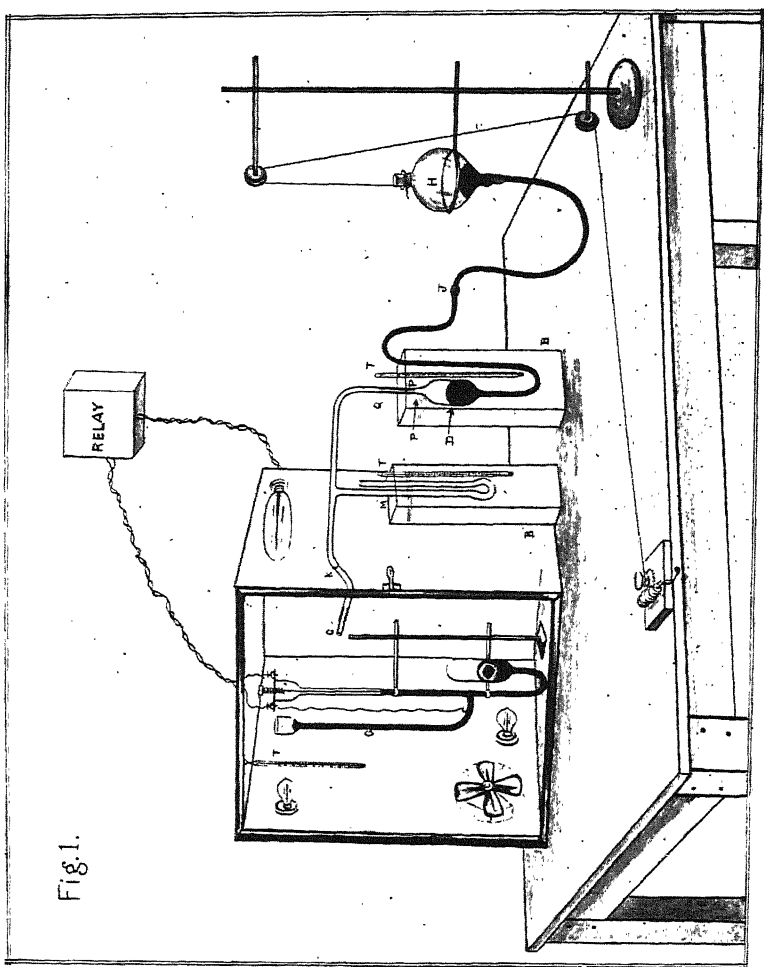


Fig. 1.

(Figure 1)

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could be maintained constant for nearly an hour. The pressure corresponding to the formation of plane surface of the meniscus was observed in the manometer by means of a travelling microscope reading accurately to the third place of decimal. Mean of several observations was taken as the true manometric height.

COMPARISON OF RESULTS.

In table, I, the values of surface tension obtained for water and benzene at two temperatures 15°C and 30°C by the above method are given along with those obtained by other workers. Table II gives the results for CaCl_2 solutions along with those of Livingston, Morgan and Schramm (J. A. C. S., 35, 1848, 1913)

TABLE I.

Surface tension of water and benzene in dynes/cm.

| Investigator | Method | Water | | Benzene | |
|--------------------|--|-------|-------|---------|-------|
| | | 15° | 30° | 15° | 30° |
| Volkman | Capillary rise Method | 73.26 | ... | 29.51 | ... |
| Domke | " | ... | 71.04 | ... | ... |
| Harkins and Brown | " | 73.55 | ... | 29.59 | ... |
| Richard and Caster | " | ... | 71.32 | 29.61 | ... |
| Ramsay and Aston | " | ... | ... | 28.68 | ... |
| Harkins and Brown | Waves on jet | 73.38 | ... | ... | ... |
| Harkins and Ching | Drop weight | ... | ... | ... | 27.61 |
| Morgan | " | ... | 71.03 | ... | ... |
| Dorsey | Waves on jet | 73.76 | ... | ... | ... |
| Sentis | Ripples | 73.45 | ... | ... | ... |
| Richard and Combs | " | 74.30 | ... | ... | ... |
| Fergusson | Jaeger's method | 72.78 | ... | 29.65 | ... |
| " | * Method (vertical capillary) | 73.88 | ... | 29.20 | 27.00 |
| " | Pressure to make meniscus plane (Horizontal capillary) | 73.47 | ... | 29.14 | ... |
| Critical Tables | (International) | ... | 71.18 | ... | 27.56 |
| Author | Present method | 73.52 | 71.21 | 29.57 | 27.59 |

* Pressure to make meniscus plane (vertical capillary).

TABLE II.

Values of Surface tension of CaCl_2 solutions compared.

| Concentration in gm. mols per 1000 gms. of water | * Livingston, R. Morgan and Schramm. Drop weight method. | Authors. |
|---|---|----------|
| 0.0 | 71.03 | 71.21 |
| 0.5 | 71.91 | 72.23 |
| 1.0 | 72.20 | 72.81 |
| 1.5 | 73.36 | 73.55 |
| 2.0 | 74.52 | 74.32 |
| 2.5 | 75.56 | 75.31 |
| 3.0 | 76.04 | 76.45 |
| 3.5 | 78.64 | 77.60 |
| 4.0 | 78.81 | 78.78 |
| 4.5 | 80.21 | 80.15 |
| 5.0 | 82.91 | 81.64 |
| 5.5 | 83.91 | 83.03 |
| 6.0 | 85.12 | 84.47 |
| 6.5 | 87.13 | 86.20 |
| 7.0 | 89.23 | 87.98 |
| 7.5 | 91.92 | 89.86 |
| 8.0 | 92.65 | 92.54 |
| 8.5 | 95.79 | 95.40 |
| 9.0 | 97.12 | 98.81 |

From the various improvements suggested in this paper the authors consider that their values are more accurate than those so far obtained by Fergusson's method. This conclusion is further supported by the fact that the values of surface tension for different solutions of calcium chloride obtained by the authors lie much closer to a smooth curve than those of Livingston, Morgan and Schramm (cf., Fig. 2).

The authors are indebted to Dr. Mata Prasad for useful suggestions which led to the use of the present improved method for determining surface tension.

* J. A. C. S., 35, 1848, 1913.

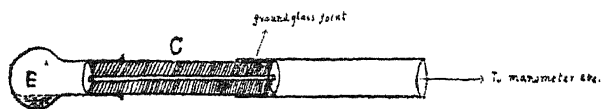


Fig. 1a.

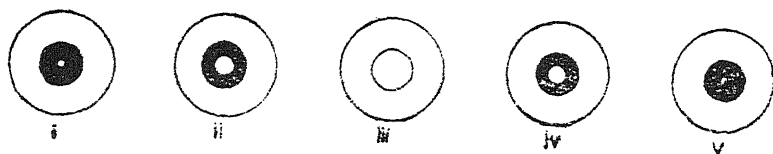


Fig. 1b.

Figs. 1a & 1b

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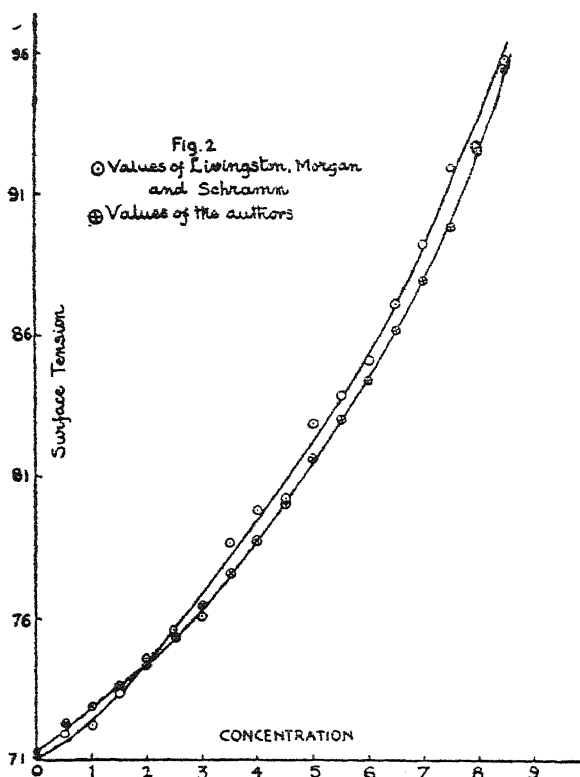


Fig. 3

Transaction No. 17: Methods of measuring Surface tension
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COAGULATION OF DILUTE OIL EMULSIONS BY MERCURIC CHLORIDE: EVIDENCE FOR THE DISCONTINUITY OF THE CHANGE IN THE SLOW REGION.

BY

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The problem of the formation and the stability of emulsions has been investigated by numerous workers from the standpoint of theory and industrial practice. One of the principal findings in this field is the importance of the data for the viscosity of the medium (Wilson, *Phil. Mag.*, 1883, 15, 406; Hillyer, *J. Amer. Chem. Soc.*, 1903, 25, 513; Marshal, *Pharm. Journ.*, 1909, 28, 264; Sanyal and Joshi, *J. Phys. Chem.*, 1922, 26, 481). It was observed by one of us (Joshi, *Trans. Farad. Soc.*, 1925, 20, 512-19) in a study of reversible emulsions that with a knowledge of this quantity, the progress of the transformation of the emulsion from one type to the other, by a mere alteration of the volume ratio of the two phases could be followed with ease and accuracy. It is known that such reversals can also be effected by the introduction of appropriate electrolytes (Clowes, *J. Phys. Chem.*, 1916, 20, 407-51; Bhatnagar, *J. Chem. Soc.*, 1921, 119, 61-8; Parsons and Wilson, *J. Ind. Eng. Chem.*, 1921, 13, 1116-23), and that analogy exists between the type reversal of an emulsion and the coagulation of a sol (Clowes, *loc. cit.* 1916, 20, 445; Bhatnagar, *Trans. Farad. Soc.*, *Symposium on Colloids*, 1920; Joshi, *loc. cit.*). Whilst a considerable mass of information is available about the coagulation kinetics of sols in the *rapid* and the *slow* region of coagulation, barring a very few exceptions (Bhatnagar, *J. Phys. Chem.*, 1921, 16, 735; Ellis, *Trans. Farad. Soc.*, 1913, 9, 14) corresponding data for emulsions are not available in the literature. In previous communications from these Laboratories (Joshi and Viswanath, *J. Indian Chem. Soc.*, 1933, 10, 329-340; Joshi and Menon, *ibid*, 1933, 10, 599-609; Joshi and Nanjappa, *ibid*, 1934, 11, 133-143; Joshi and Iyengar, *ibid*, 1934, 11, 555-571; 573-577; Joshi and Pannikar, *ibid*, 1934, 11, 797-804), it has been shown that the process of the *slow* coagulation of a number of sols produced by variously concentrated solutions of different electrolytes, and by oppositely charged sols is not continuous with respect to the coagulation time. Since this conclusion constitutes a departure from the

current theories of the kinetics of coagulation, it was of interest to examine it for the *slow* coagulation of a different class of colloids, *viz.* emulsions.

Evidence has been presented previously (*loc. cit.*) that any one of the familiar properties used to measure the degree of coagulation is restricted in the range of its applicability. In the following experiments, therefore, completer information was sought by employing three independent methods in order to follow the progress of a coagulation, *viz.*, viscosity, transparency and refractive index. With the exception of a communication to the Chemistry Section of the *Proc. Ind. Sci. Congress* 1934, from these Laboratories, the use of variation in the last mentioned property as a measure of coagulation does not appear to have been recorded in the literature of the subject. The application of this method, studied in numerous cases in these Laboratories, has revealed the presence of factors which were not noticed in results with earlier methods of measuring coagulation.

EXPERIMENTAL.

The emulsions were prepared by the precipitation method as developed previously (Joshi, *Koll. Zeit.*, 1923, 34, 197-201). Briefly, about 1.5 c.c. of the purest available sample of the oil to be emulsified was dissolved in a small amount of absolute alcohol. This solution was then poured in about a litre of twice distilled water which was almost boiling hot. After vigorous shaking, a fine, bluish grey emulsion, uniformly dispersed, was obtained. Free alcohol was removed by boiling off carefully. It was then passed through a double filter paper of close texture and stocked in Jena glass bottles. Thus prepared the emulsions are very stable, except for 'creaming' which depends principally on the difference in the specific gravities of the two component liquids. This, however, is a very slow process and is practically negligible. By far the majority of experiments reported here were made with emulsions from the *Til* oil. Emulsions used in experiments to which the viscosity-time curves Nos. 10, 11 in fig. 2 refer, were made with mustard oil.

The viscosity was measured by Scarpa's method (*Gazetta*, 1910, 40, 271; *cf.* also Farrow, *J. Chem. Soc.*, 1912, 101, 347) with modifications described previously (Joshi and Menon, *loc. cit.*). Using a small capillary with a bulb at one end, the method requires but a knowledge of t_1 , the time of rise of a small amount of the liquid to be studied under constant suction, and t_2 , the time for fall under its own hydrostatic pressure. No knowledge of the density of the liquid is required, which is a great advantage. The suction applied was kept constant at 25 ± 0.05 cm., water, the observations being made with a low

power telescope. The temperature of the thermostat was $35 \pm 0.1^\circ\text{C}$. Equal volumes of the emulsion and of the electrolyte solution of the required strength were allowed to attain the temperature of the thermostat. The coagulation was started by mixing the liquids in the Scarpa tube V (*cf.* fig. A, Joshi and Viswanath, *loc. cit.*). The viscosity of the mixture was then measured at convenient intervals for about four hours; in a few cases the observations were continued to about 24-48 hours after the start of the coagulation. In all the coagulations studied previously (*loc. cit.*) viscosity measurements were continued till the coagulating sol in the capillary or the bulb of the viscometer showed the least traces of flocculi. This was not possible in the present work despite special arrangements made and precautions taken for the observation of any heterogeneities produced during coagulation. This was at least partly due to the relative optical characteristics of the oils emulsified and water. η , the viscosity was calculated from the formula, $\eta = K \frac{t_1}{t_1 + t_2}$, where K is a

constant. The value of K was calculated from t_1 , t_2 measurements made with a standard liquid like water for which η is known to be 0.7225 C. P.; the results are therefore in absolute centipoise units. The degree of the reproducibility of results using pure liquids was found to be at least 3-4 in 1000. Variations less than at least 4 times this value were not considered. These results are shown graphically in figs. 1-2. In order to economise space and also to prevent curves from coalescing, the scale units and the position of the origin were varied in a group of related curves, and have been indicated in figures.

Measurements of the transparency during coagulation were made by the use of a sensitive thermopile and a low resistance Broca galvanometer. Light from a 4-volt lamp run at a constant potential from a battery of storage cells was first passed through a column of distilled water in order to cut out the heat radiation, and then allowed to fall on the optical cell which contained the coagulating mixture. Intensity of the light transmitted by the sol was indicated by the deflections of the galvanometer. The source of light, the water filter, the coagulating sol and the thermopile were enclosed in an air thermostat with glass sides. This was immersed in water in another thermostat, except on the top which was closed by a well fitting cover insulated against heat conduction by thick pads of sheep wool. The outer thermostat was also well protected by pads of wool except on the glass faces which were well screened to cut off stray light. The temperature of this thermostat was kept constant at $32.6 \pm 0.2^\circ\text{C}$. Under these conditions the thermopile was found to be well protected against external radiation and changes of temperature. In order to

compare coagulations with mercuric chloride with other coagulants, typical curves with dilute solutions of cadmium chloride and sulphuric acid are also given. These results for the transparency are shown by time-deflection curves in fig. 3.

The refractivity measurements were made with the Pulfrich refractometer. By means of water circulation from a thermostat the temperature of the glass cell in the refractometer which contained the liquid to be examined was brought to 34°C . From samples of the emulsion and of the solution of the coagulating electrolyte, which were also preheated to $34^{\circ} \pm .1^{\circ}\text{C}$, exactly one c. c. of the emulsion and then an equal amount of the coagulant were introduced carefully in the refractometer cell, and the mean time of addition noted. Measurements were continued till the readings became constant. Curves 1-7 in fig.4 relate μ , the refractive index with the coagulation time. Three stocks of *Til* oil emulsion A, B, C were used with approximately the same oil content. Curves 1-6 in figs.1 & 2, curves 7, 8 in fig-2, and curve 9 in fig-2 and all curves in figs.3 and 4, refer to experiments made with stocks A, B, C respectively. Curves 10 & 11 in fig.2 refer to mustard oil.

DISCUSSION OF RESULTS.

An examination of the viscosity-time curves in figs. 1 and 2 confirms the conclusion drawn previously from the coagulation data of a number of sols by a variety of coagulants (*loc. cit.*) that the progress of coagulation, in so far as change of viscosity is a measure of the corresponding degree of coagulation produced, is not continuous with coagulation time, and that the occurrence of breaks or discontinuities tends to be more pronounced the lower the concentration of the electrolyte. It is also seen that in the majority of coagulations studied (*cf.* figs. 1,2) and in agreement with earlier results (*loc. cit.*) that the course of coagulation is marked by an initial diminution of viscosity variable in the range 0.6 to 2 per cent of the initial viscosity. Small alterations in the concentration of a coagulator are known to have a marked effect on the time required for attaining a given stage of coagulation (*cf.* Joshi and Viswanath, *loc. cit.*). This is also to be anticipated from Paine's exponential relation relating the coagulation velocity and the electrolyte concentration (*Koll. Chem. Beih.*, 1912, 16, 430); it is interesting therefore, to note that the time corresponding to the occurrence of this initial diminution of viscosity varies irregularly in the range 20 to 30 minutes after the start of the coagulation despite appreciable variations in the concentration of the coagulator. These results are similar to those obtained previously with *hydrophobes* (*cf.* Joshi and Viswanath, Joshi and Iyengar, *loc. cit.*) and are in agreement with the suggestion made earlier (Joshi and

Pannikar, *loc. cit.*) that the period corresponding to the initial diminution of viscosity might not be a stage in the main process of coagulation, envisaged as a continuous coalescence of particles into aggregates of increasing size. It might be mentioned incidentally, that this is the main mechanism implied in Smoluchowski's theory of the kinetics of coagulation (*Z. Phys. Chem.*, 1917, 92, 129).

It has been in general tacitly assumed by colloid chemists that coagulation necessarily produces a *nett* rise in the viscosity. That this is by no means always true is shown by curves Nos. 2, 3, 4 in fig. 1 and curve No. 6 in fig. 2. The last shows a definite and a marked *diminution* of viscosity below the initial value as a result of the coagulation. Very definite instances of an overall and appreciable decrease in viscosity consequent upon coagulation of lyophobic colloids were observed earlier (Joshi and Nanjappa, Joshi and Iyengar Joshi and Pannikar, *loc. cit.*). It is probable that the occurrence of the initial diminution of viscosity mentioned already and the overall decrease in viscosity due to coagulation might result, in part, from the operation of the same factors. While more detailed and wider based experimental results are necessary for their satisfactory elucidation, the generality of the above findings is a clear evidence of the theoretical deficiency in the present position of the viscosity of colloids.

Results shown by curves in fig. 3 show a diminution of transparency during coagulation, which is to be anticipated on general grounds. With the exception of curve 3, it is seen that, the change is rapid in the initial stages and almost comes to a standstill during later stages. From a general comparison of this last mentioned period with the corresponding sections of the viscosity-time curves, which almost as a rule are characterised by discontinuities, the possibility is suggested that transparency measurements might not be susceptible to changes revealed by a typical colloid sensitive property like viscosity. Some observations of the transparency and the viscosity measurements of a number of protected colloids subjected to coagulation studied in these Laboratories (Joshi and Joga Rao, *J. Indian Chem. Soc.*, 1933, 10, 247) were amongst the earliest evidences in this line.

An examination of results in fig. 4 shows that the refractive index of a coagulating sol diminishes during coagulation in all the cases and this tendency is greater the greater the concentration of the coagulator. It is interesting to see from these curves that the above change occurs through stages during some of which the refractivity remains sensibly constant. It would also appear that the number of such stages tends to increase as the electrolyte concentration is

Fig. 1
Variation of Viscosity during Coagulation.

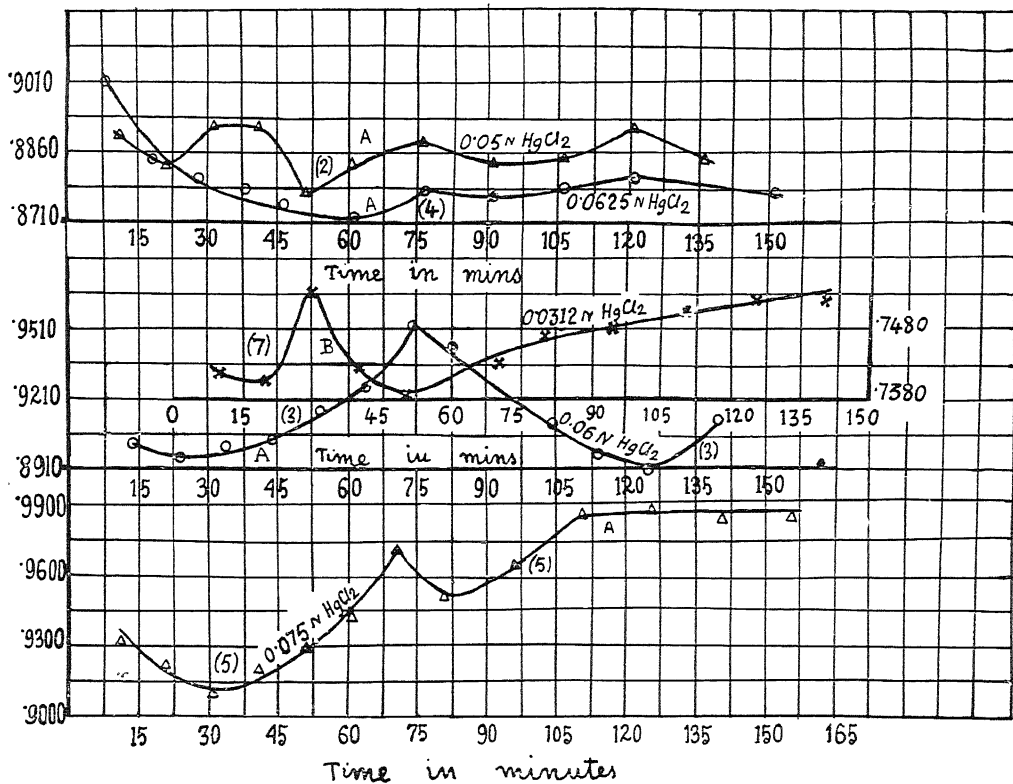


Fig. 2

Variation of Viscosity during Coagulation.

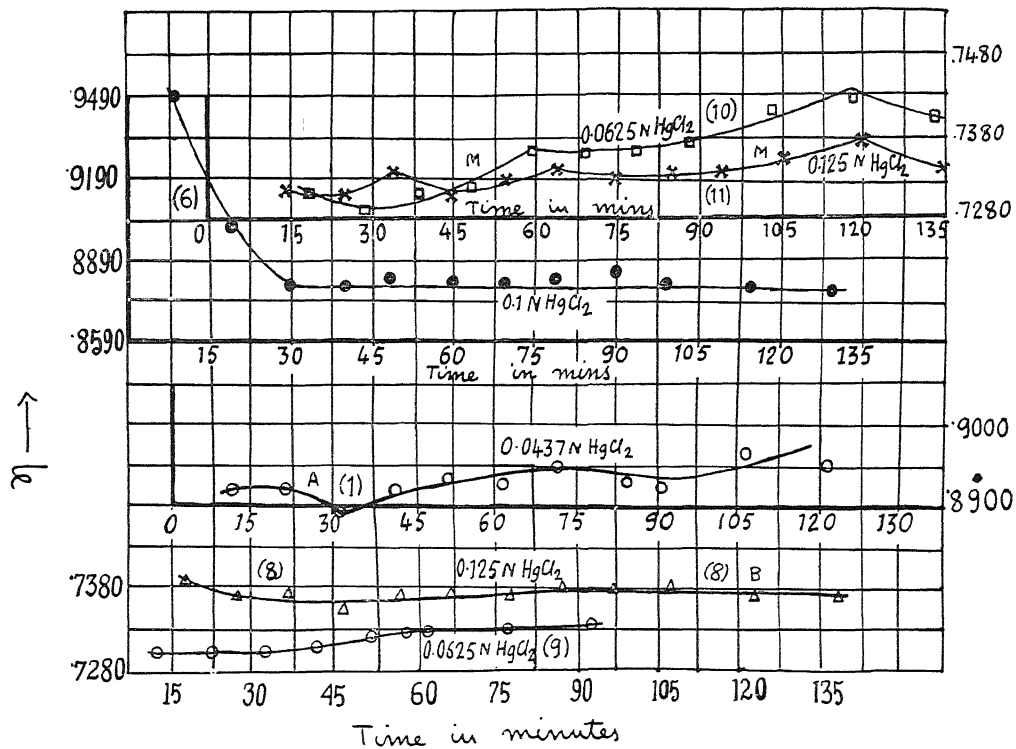
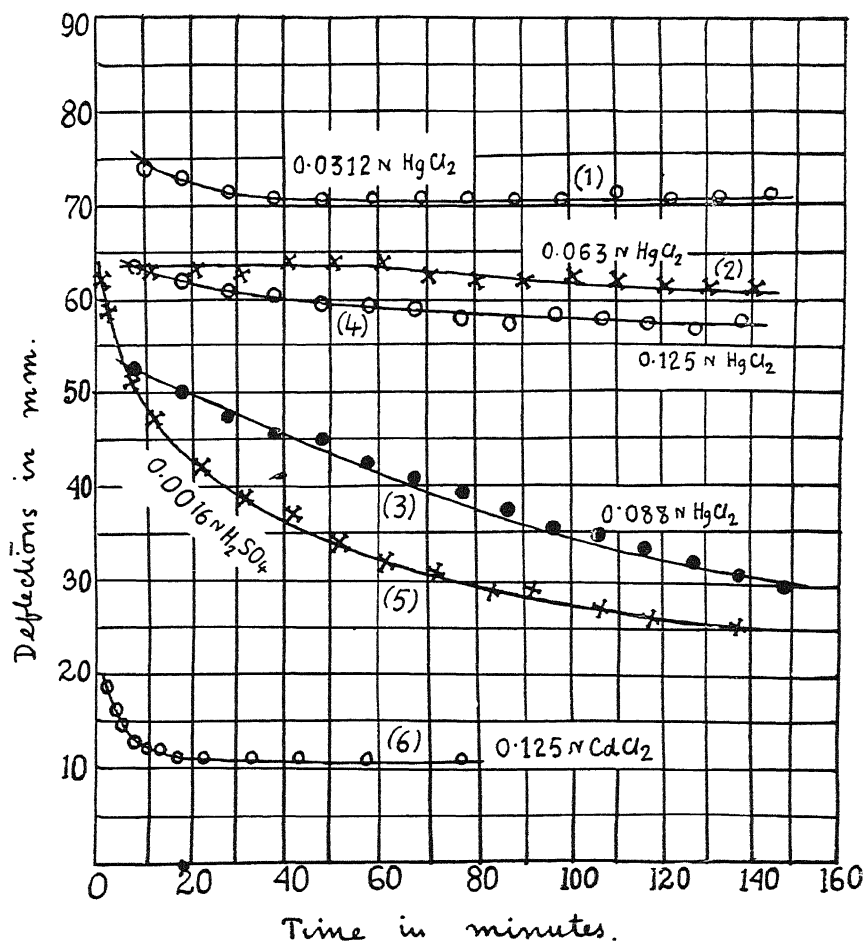


Fig. 3(c)
The Variation of Transparency
during Coagulation



increased. Despite notable contributions to the subject (Rayleigh, *Phil. Mag.*, 1871, 41, 107; 1899, 47, 375, *et seq*; Garnett, *Phil. Trans.*, 1904, (A) 203 385; 1906, 237; Mie, *Koll Zeit.*, 1907, 129; *Ann. der Phys.*, 1908, 25, 337; Lampa, *Akad. Wiss. Wien. Sitz. Ber.* 1909, 118, 867-83), the prevalent theories of the optics of the colloid state do not yet allow of an *a priori* analysis of the refractivity of a coagulating sol in terms of the composition of the system; the refractive index of the coagulating material, the dispersion medium and of the dispersed phase; the micellar charge; the size, (shape) and the number of the particles per unit volume, and so forth. Changes in the last named factors produced during coagulation alter the magnitude of the total optical path which a ray of light traverses in unit time in the system and therefore its overall refractivity. It is anticipated therefore that the refractivity of the system should, during the process of coagulation, approximate to that of the continuous medium modified by the presence of the coagulant. The results obtained are in agreement with this deduction only partially, since size and the number of particles per unit volume are not the only determinants of the refractivity of the system, liable to change during coagulation. The remarkable result that in at least a definite number of cases the refractivity remains constant for a period, and then changes *discontinuously* to a new value also characterised by a similar constancy for a time, and so on throughout the progress of coagulation, observed for the first time in these Laboratories, not only supports the view developed previously that coagulation constitutes a complex succession of micellar and allied changes in the dispersion medium, but also that the property selected for measuring coagulation might not be sensitive at a given stage to some or all of the above changes constituting coagulation. If for instance, this happens during the initial stages of coagulation, the so called S-shape in the corresponding coagulation-time curve would result, and give but a spurious evidence of *autocatalysis*. It would certainly be of interest from the standpoint of a comprehensive theory of coagulation to investigate if the occurrence of discontinuities, each marked by a constant value of the refractivity is a *general* phenomenon. That it is certainly very widely occurrent, though hitherto unrecognised, is almost a foregone conclusion from data accumulated already in these Laboratories from observations of over sixty cases.

CHEMICAL INVESTIGATION OF THE SEEDS OF HYGROPHYLLA SPINOSA.

BY

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Hygrophylla Spinosa is a herb abundant throughout India. It is very common in the Konkan. It belongs to the natural order Acanthaceae. The vernacular names are :—

Kokilaksha, or Ikshugandha, (Sanskrit).; Talimkhana, (Hindi); Niramalli, (Tamil); Kuliamera, (Bengali) Ekharo (Gujarathi); Kolsundara, (Marathi).

It is an annual marshy herb having bright purple flowers. The seeds are small, flattish and brown in colour, like the eyes of Indian Cuckoo from which it derives its Sanskrit name Kokilaksha. The roots and the seeds are widely used in Indian medicine. The root is considered cooling, bitter, tonic, and is used in rheumatism, urinary affections, and anasarca. Dr. Gibson recommends its use as a diuretic. Mohamedan physicians consider the seeds as aphrodisiac. In Unani medicine the seeds are given in gonorrhoea and with milk and sugar in spermatorrhoea. The peculiarity of the seeds is that when they are placed in the mouth or water they become immediately coated with a large quantity of extremely tenacious mucilage.

The roots of this drug have been investigated by Warden (Pharmacographia Indica vol. III page 38), and by Ghatak and Dutt (Jour. Ind. Chem. Soc. 1931, 23). Warden found in the seeds traces of an alkaloid and 23 per cent. of a fixed oil. Ghatak and Dutt found in the roots a sterol which they termed Hygrosterol.

The present investigation was undertaken with a view to submit the seeds to a thorough and systematic examination. We did not find any alkaloid nor Hygrosterol. A pale yellow fixed oil was obtained in 21 per cent. yield. This oil belongs to the type of semi-drying oils. The solid acids of this oil have been shown to be myristic, palmitic and stearic acids only. The presence of linolic acid has been shown in the liquid acids. The other acids present in the liquid acids are at present unknown.

EXPERIMENTAL

Moisture :—The percentage of moisture in the average sample of the seeds was determined by heating a weighed quantity at 100°C. The percentage loss was 8.43.

Ash :—A weighed amount of the seeds was incinerated and the percentage of ash was found to be 10.2. It was analysed qualitatively and was found to contain potassium, phosphorous and trace of iron.

Test for Enzymes :—50 grms. of the ground material were soaked in water and kept overnight in a corked flask. Next day the mass was swollen and the cork was blown out due to the immense pressure mostly of Carbon dioxide. The top aqueous layer was filtered. The filtrate was found to contain a reducing sugar, thus proving the presence of enzymes in the seeds.

Test for alkaloids :—50 grms. of the powdered seeds were digested with Prolius' fluid. The filtrate on being examined in the usual manner for the presence of alkaloids, gave negative results.

Tests for Starch, tannins etc. :—10 grms. of the seeds were treated with 100 c.c. of distilled water and warmed on the water bath for half an hour. The mixture was then filtered and the filtrate when tested for (1) starch with dilute iodine solution indicated its absence, (2) tannins with ferric chloride indicated its absence, (3) reducing sugar with Fehling's solution showed its absence.

Test for volatile oil :—100 grms. of the material were distilled with steam and about 500 c.c. of the distillate were collected. The latter was not acidic nor was it found to contain any volatile oil.

Extraction with different solvents :—In order to ascertain the general character of the constituents 50 grms. of the ground material were successively extracted in a soxhlet apparatus with different solvents. The percentage of extracts dried at 100° and the nature of extracts are given in table I.

TABLE I.

| | Solvent used | per cent. of extract | nature of extract |
|-----|-----------------|----------------------|-----------------------------|
| (1) | Petroleum ether | 21 | A pale yellow oil |
| (2) | Ether sulphuric | 1.06 | A dark red semi-solid mass. |
| (3) | Chloroform | 0.5 | A reddish black liquid. |
| (4) | Alcohol | 8.87 | Thick resinous mass. |

Investigation of the oil :—6 lb. of the seeds were extracted in a soxhlet apparatus with petroleum ether B.P. 60° to 80°. The petroleum ether was removed on the water bath and the resulting oil was

kept in a vacuum desiccator over solid paraffin wax to remove the last traces of petrol. The oil thus obtained was used for all the work detailed below. It had a pale yellow colour and sweet taste like an edible oil. It was free from nitrogen and sulphur. The physical and chemical constants were determined by standard methods and are given in table II.

TABLE II.

Analytical constants of the oil from *Hygrophyla Spinosa*.

| | | |
|-----|----------------------------|---------------|
| (1) | Density at 30° | 0.9254 |
| (2) | Refractive index at 33° | 1.469674 |
| (3) | Iodine Value Wijs's method | 122.1 |
| (4) | Saponification Value | 206.5 |
| (5) | Acid Value | 2.65 |
| (6) | Unsaponifiable matter | 7.5 per cent. |
| (7) | Reichert Meissl Value | 0.25 |
| (8) | Polenske Value | 0.46 |
| (9) | Acetyl Value | 39.4 |

Mixed fatty acids :—150 grms. of the oil were saponified with alcoholic caustic soda solution. The dry soap was then extracted with petroleum ether to remove the unsaponifiable matter. The soap was then decomposed with dilute sulphuric acid and the liberated fatty acids were separated, washed and dried. The mixed fatty acids had the constants shown in table III.

TABLE III.

| | | |
|-----|-------------------------|---------|
| (1) | Titre test | 28.85° |
| (2) | Melting point | 32.2° |
| (3) | Neutralisation value | 190.17 |
| (4) | Mean molecular weight | 295.3 |
| (5) | Iodine value | 125.8 |
| (6) | Refractive index at 33° | 1.46264 |

The mixed fatty acids were then separated into the solid and liquid acids by Twitchell's lead-salt alcohol method. (J. Ind. Eng. Chem. 1921, 18, 806). 20 grms. of the mixed fatty acids were dissolved in 250 c.c. of 95 per cent. by volume of alcohol. 20 grms. of lead acetate were dissolved in 250 c.c. of alcohol. Both were heated to boiling and then mixed and allowed to cool to room temperature. It was kept at 15° for several hours. The precipitated lead salts were filtered and washed with 100 c.c. of cold alcohol. From the combined filtrates alcohol was removed on water bath in a current of carbon dioxide. The remaining lead salts were taken up in ether, decomposed with dilute nitric acid, the ether layer was washed with water till free from mineral acids, dried over anhydrous

sodium sulphate and ether removed in a current of carbon dioxide. The liquid acids thus obtained are termed liquid acid I. The lead salts of the solid acids were again dissolved in 250 c.c. of alcohol containing, 1 c.c. of acetic acid. The solution was cooled and kept at 15° for several hours. The precipitated lead salts were filtered and washed with little alcohol. The free solid acids were obtained from the lead salts in the usual way. From the filtrate the liquid acids were recovered as described above and are termed liquid acid II. The results of two separations is given below.

| | Weight of the mixed acids | Liquid acid I | Liquid acid II | Solid acids. |
|----|---------------------------------|---------------|----------------|--------------|
| I | 20 grms. | 12.0 grms. | 2.7 grms. | 4.9 grms. |
| II | 40 grms. | 23.0 grms. | 5.1 grms. | 9.8 grms. |

The percentage of the liquid and the solid acids in the mixed fatty acids is therefore :—

Liquid acids 75 per cent.

Solid acids 25 per cent.

The constants of the solid and liquid acids are given in table IV

TABLE IV.

| Constants | Solid acids | Liquid acids I | Liquid acids II |
|-------------------------|-------------|----------------|-----------------|
| Iodine Value | 7.0 | 143.0 | 139.0 |
| Neutralisation Value | 211 | 190.3 | 184 |
| Mean molecular weight | 265.8 | 294.8 | 305 |
| Melting point | 60° | | |
| Refractive Index at 30° | — | 1.47125 | 1.46977 |

Solid acids :—The saturated acids were esterified by the Fischer Speier method by boiling for 4 hours with four times their weight of methyl alcohol containing 5 per cent. of dry hydrogen chloride. The esters were poured in water and extracted with ether. The ether solution was washed with a solution of sodium bicarbonate to remove any unesterified acids. The ether extract was dried over sodium sulphate and the esters recovered. They were then fractionated in modified Claissen flask at 4 m.m. pressure. The results are given in Table V.

TABLE V.

Fractional distillation of 30.5 grms. of the methyl esters of solid acids at 4 m.m. pressure.

| No. of fraction | B. P. in degrees C | Wt. in grms. | Saponification Value | Mean molecular weight |
|--------------------|-----------------------|--------------|-------------------------|--------------------------|
| I | below 155 | 0.15 | — | — |
| II | 155–160 | 4.12 | 217.0 | 258.5 |

| | | | | |
|---------|---------|-------|-------|-------|
| III | 160-165 | 4.45 | 204.5 | 274.3 |
| IV | 165-170 | 14.76 | 204.4 | 274.5 |
| Residue | — | 6.77 | 198.3 | 284.0 |

The first fraction was almost alcohol and was therefore neglected. Fraction 2. This was a mixture of palmitic and myristic esters. The ester was hydrolysed and the resulting mixture of acids was crystallised from alcohol when a small quantity of myristic acid M.P. 53° and M. W. 228 was isolated. Hence assuming this fraction to consist of methyl myristate and methyl palmitate the composition of this fraction is:—

| | |
|------------------|----------------|
| Methyl myristate | 41.1 per cent. |
| Methyl palmitate | 58.9 per cent. |

Fraction 3. This was a mixture of palmitic and stearic esters. The mixture of acids obtained on hydrolysing this fraction was purified by the fractional precipitation of the magnesium salts. The acids were just neutralised with KOH in alcoholic solution and magnesium acetate solution added just enough to precipitate one-third of the total acids. The precipitated magnesium salts were filtered and the acid recovered from them. This on crystallisation from alcohol had M.P. 69° and M.W. 284. and was identified as stearic acid by mixed M.P. with an authentic specimen. The acid recovered from the more soluble magnesium salts had M. P. 62°C and M.W. 256. and was identified as palmitic acid. The composition of this fraction is Methyl palmitate 84.64 per cent. and methyl stearate 15.36 per cent.

Fraction 4. This was similar to the above fraction and consisted entirely of methyl palmitate and methyl stearate. The composition of this fraction is methyl palmitate 83.93 and methyl stearate 16.07 per cent.

Residue. The M. W. suggests that no acid higher than stearic acid can be present and actually none was isolated. On the assumption that this fraction consists of palmitic acid and stearic acid only the composition is methyl palmitate 50 per cent. and methyl stearate 50 per cent.

Therefore the composition of the solid acids is,

| | |
|---------------|----------------|
| Myristic acid | 5.5 per cent. |
| Palmitic acid | 73.0 per cent. |
| Stearic acid | 21.4 per cent. |

Unsaturated acids.

The liquid acids were examined by the bromine addition method of Jamieson and Baughman (J. Amer. Chem. Soc. 1920, 42, 2398),

The acids were dissolved in 100 c.c. of ether and cooled, and a cold solution of bromine in ether was added. It was kept at 0° for four hours. No precipitate of hexabromide was obtained. It is definite, therefore, that linolic acid was absent in the unsaturated acids. The solution was washed with a solution of sodium thiosulphate to remove the excess of bromine, dried over sodium sulphate and ether distilled off. The residue was dissolved in 150 c.c. of petroleum ether (B. P. 60°–65°) and kept in an ice bath for two hours. The precipitate of tetrabromo stearic acid was filtered through a gooch crucible and the filtrate concentrated. The precipitate obtained on cooling the solution was filtered through the same gooch. The weight of tetrabromo stearic acid, its M.P. and the bromine content were determined. From the filtrate the solvent was removed and the weight and the bromine content of the residue were ascertained. The results of bromination of the liquid acids I and liquid acids II are recorded below.

Bromination of liquid acids I.

| | | |
|--|-----------|-----------|
| Weight of acid taken | = 3.8623 | gms. |
| Weight of tetrabromo stearic acid | = 2.19 | gms. |
| Per cent. of Bromine in the above | = 53.36 | |
| M.P. of tetrabromo stearic acid | 112°–113° | – |
| Weight of the residue of di-and tetra-bromo acids. | 4.963 | gms. |
| Bromine content of the residue | = 41.76 | per cent. |

Bromination of liquid acids II.

| | | |
|--|----------|------|
| Wt. of acids taken. | 1.1156 | gms. |
| Wt. of tetra bromostearic acid | = 0.1991 | gms. |
| Per cent. of bromine in the above compound | 53.34 | |
| M.P. of tetra bromo stearic acid | 113° | |
| Wt. of the residue | 1.6827 | gms. |
| Per cent. of bromine in the residue | 40.68 | |

The M.P. and the bromine content of tetrabromo acid confirms the presence of linolic acid in the liquid acids. The molecular weight of liquid acids (compare table IV) indicates the presence of an acid of high molecular weight. Erucic acid cannot be present because the bulk of it would have remained in the solid acids in the separation of the solid and liquid acids by lead salt alcohol method as shown by Sudborough, Watson and Damle (Jour. Ind. Inst. of Science 1926, Vol. 9 A, part II page 29). The iodine value of the solid acids shows that erucic acid is not present to any considerable extent in the solid acids. Oxidation of liquid acids was carried out with a view to find out the presence of oleic acid and the other unsaturated acid of high

molecular weight, but the results were not conclusive. Hence at present the composition of the liquid acids cannot be calculated.

Unsaponifiable matter.—It was obtained by extraction of the dry soap with petroleum ether. On twice crystallisation from alcohol it had the m.p. 114–115° C. It gave all the colour reactions of phytosterol. Though the amount of the unsaponifiable matter in the oil is considerable (viz. 7.5 per cent.) still most of it was a gummy mass, only a small fraction being obtainable in the crystalline state. Hence it was not possible to characterise the sterol present in the unsaponifiable matter.

With a view to throw light on the nature of the unsaturated acid of high mol. wt. present in the oil experiments on the hydrogenation of the oil are in progress.

We thank Dr. M. S. Shah, Head of the chemistry department for facilities.

CONDENSATION OF PHENOLS AND PHENOLIC ETHERS WITH ACETONE DICARBOXYLIC ACID.

PART II.

β-Substituted cyclobutenone carboxylic acids.

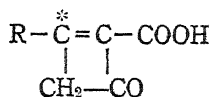
BY

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It has been shown in part I of this series (J. Ind. Chem. Soc. 1931, VIII, 787) that, phenol, anisol and *o*-cresylmethyl ether condense with acetone dicarboxylic acid, each giving a para substituted (1) glutaconic acid and (2) monobasic ketonic acid.

This latter compound was obtained in greater quantity by (1) immediate crystallisation of the product precipitated on pouring the reaction mixture of phenol and acetone dicarboxylic acid into ice; (2) heating the corresponding para substituted glutaconic acid at its m. pt. and (3) heating the glutaconic acid with acetyl chloride. The new acid changed to the glutaconic acid in moist air and in dilute alcohol, which was regarded as hydrolysis since, the new acid, on analysis, was found to contain one molecule of water less than the corresponding glutaconic acid. The hydrolysis was hastened with alkali and stopped in desiccator as usual. The new compound is supposed to be a β-substituted cyclobutenone carboxylic acid of the general formula :—

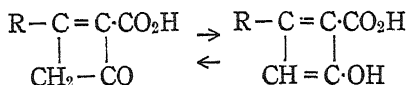


On submitting the new compound to several reactions, the following experimental results were obtained :—

- (1) Each of the new compounds titrated as a monobasic acid and formed a stable barium salt.
- (2) The new acid formed a monoacetyl derivative which could be titrated as a monobasic acid. A diacetyl derivative was obtained when there was a free—OH group in R.

(*C being in the para position with respect to the hydroxy or the methoxy group in R.)

- (3) The new acid gave a monochloro derivative with phosphorous trichloride. The monochloro compound titrated as a monobasic acid.
- (4) The new compound yielded a monosemicarbazone and a mono hydrazone.
- (5) The new acid also formed a mono isonitroso derivative. The enolic and ketonic action of the compounds can be accounted for by the tautomeric formula :—



According to Bland and Thorpe (Trans, Chem. Soc. 1912, 107, 859) action of acetyl chloride on β -phenyl glutaconic acid produced an anhydride which was however found to behave in the same way as described under (1) and (3) with respect to titration and action of phosphorous trichloride. These reactions which are not expected from a normal anhydride were explained by them on the assumption of the mobility of a hydrogen atom in the methylene group in the normal anhydride and its consequent transformation into a stable hydroxy

anhydride of the formula :— $\text{R}-\text{C} \begin{array}{l} \text{CH}-\text{CO} \\ \swarrow \quad \searrow \\ \text{CH}=\text{C}(\text{OH}) \end{array} \begin{array}{l} >\text{O} \\ \text{O} \end{array}$

They were not able to obtain the normal anhydride of β -phenyl glutaconic acid.

Their formula of a hydroxy anhydride however falls short to explain reactions Nos. (2), (4) and (5) mentioned above, manifested by the compounds isolated in this work; the formula of β -substituted cyclobutenone carboxylic acid seems to explain all reactions described above in a satisfactory manner. Besides, the formation of a hydroxy anhydride has not been conclusively established by Thorpe and his co-workers and the conversion of the two types of anhydrides into one another has not been reported.

EXPERIMENTAL.

α -Carboxy- β -(4-hydroxyphenyl) cyclobutenone, from

(a) *phenol and acetone dicarboxylic acid* :—The reaction was carried out exactly as given in part I. The flocculent precipitate obtained by pouring the reaction mixture on ice was quickly separated on cotton wool and washed with a small quantity of alcohol. The mass of cotton wool was transferred to a beaker and the adhering product was crystallised from absolute alcohol, quickly dried and kept in a sealed tube: yellowish silky needles m.p. 224° ;

yield, 20%. (Found: Equivalent wt., 203.7; C, 64.66; H, 3.85. $C_{11}H_5O_4$ requires Eq. wt., 204; C, 64.7; H, 3.93 per cent.) *Barium salt* precipitated from a dilute alcoholic solution of the acid by barium acetate. (Found: Ba, 25.4; $(C_{11}H_7O_4)_2$ Ba requires Ba, 25.23 per cent.)

(b) *From β -4-hydroxyphenylglutaconic acid by (i) heating it at its m. pt.*:—The pure glutaconic acid (5 g.) was heated in a hard-glass tube in a paraffin bath at 195° for 45 minutes under a drying tube and cooled. The solid residue gave yellowish needles from absolute alcohol: m.p. 224° ; yield, 60%. Mixed with the compound in (a) m.p. 223° .

(ii) *By the action of acetyl chloride*:—The glutaconic acid (5 g.) was refluxed with acetyl chloride (10 c.c.) in a dry atmosphere on a water-bath for 2 hours. The acetyl chloride was evaporated and the residue extracted with ether. The ethereal solution was shaken with sodium bicarbonate solution which was then separated. This alkaline solution on acidifying deposited a sticky mass which solidified with alcohol in the refrigerator and gave yellow crystals from absolute alcohol: m.p. 224° ; yield, 20%. Mixed with the compound in (a) m.p. 224° . Pinkish needles of the diacetyl derivative (m.p. 123°) were obtained from the mother liquor after 24 hours.

Hydrolysis of α -carboxy- β -(4-hydroxyphenyl)-cyclobutenone—by 10% solution of sodium hydroxide gave theoretical yield of β -4-hydroxyphenyl glutaconic acid: prismatic crystals m.p. 184° with decomposition. Mixed with the synthetical glutaconic acid of part I: m.p. 183° with decomp.

The diacetyl derivative:—This was obtained by heating the cyclobutenone acid (2 g.) with acetic anhydride (10 c.c.) and fused sodium acetate in a protected reflux for half an hour and pouring the reaction mixture into ice. The product solidified in contact with alcohol and gave pink leaflets from acetone and chloroform: m. p. 122° , yield, 70%. Mixed with the said diacetyl derivative of (b ii): m. p. 123° . (Found: Eq. wt., 286.9; C, 62.43; H, 4.21. $C_{15}H_{12}O_6$ requires Eq. wt., 288; C, 62.5; H, 4.16 per cent.). *Barium salt* crystallised from dilute alcohol. (Found: Ba, 19.25. $(C_{15}H_{11}O_6)_2$ Ba requires Ba, 19.32 per cent.).

The monochloro derivative:—This was prepared by heating the cyclobutenone acid (5 g.) with phosphorous trichloride (12 c.c.) under a protected reflux on a water-bath for two hours. The cooled mixture was poured over ice and the pasty mass which separated, was extracted with sodium bicarbonate solution and filtered. The

filtrate, on acidifying, gave a brownish powder which formed green rhombic plates from ethyl acetate: m. p. 143° ; yield, 20 %. (Found: Eq. wt., 222.14; Cl, 15.81. $C_{11}H_7O_3Cl$ requires Eq. wt., 222.5; Cl, 15.95 per cent.).

The monosemicarbazone:—This was obtained by shaking the solution of the cyclobutenone acid (2 g.) in absolute alcohol (20 c.c.) with semicarbazide chloride: Long white needles from ethyl acetate m. p. 258° with blackening. (Found: Eq. wt., 260; N, 16.2. $C_{12}H_{11}O_4N_3$ requires Eq. wt., 261; N, 16.1 per cent.).

The monohydrazone:—This was obtained by shaking a solution of the cyclobutenone acid in absolute alcohol with phenyl hydrazine hydrochloride and fused sodium acetate: Long yellow needles from chloroform, m. p. 193° . (Found: Eq. wt., 292.5; N, 9.52 $C_{17}H_{14}O_3N_2$ requires Eq. wt., 294; N, 9.5 per cent.).

The mono-isonitroso derivative:—This was obtained by warming a mixture of the cyclobutenone acid (2 g.), pure sodium nitrite (1 g.) and sodium acetate solution (20 c.c. of 10%) and pouring the mixture into ice cold acetic acid (25 c.c. of 20%). The brown powder which separated, formed red prisms from ethyl acetate: m. p. 201° with blackening; yield, 20%. (Found: N, 5.9. $C_{11}H_7O_5N$ requires N, 6.00 per cent.).

Table No. I (compounds from acetyl derivative of phenol.)

| Name. | Formula. | Method of formation and yield. | Appearance and m.p. or b.p. | Analysis. | |
|--|----------------------|---|---|-------------------------------------|-------------------------------------|
| | | | | Calc. | Found. |
| 1. α -Carboxy- β -4-acetoxyphe- nyl cyclobutene. | $C_{13}H_{10}O_5$ | Heating the corr. glutaconic acid with (1) acetyl chloride and (2) at its m. pt. Yield 25%. | Colourless needles; m.p. 171°. | Eq. wt., 246. C, 63.4 H, 4.06 | Eq. wt. 244.5 C, 63.5 H, 3.98 |
| 2. Acetyl derivative of (1) ... | $C_{16}H_{12}O_5$ | Heating (1) with acetic anhydride; yield, 45%. | Pink leaflets; m.p. 122°; identical with the diacetyl derivative of α -carboxy- β -4-hydroxyphenyl cyclobute- none. Mixed m.p. 123°. | | |
| 3. Monochloro derivative ... | $C_{13}H_9O_4Cl$ | Heating (1) with PCl_5 ; yield, 40% | Greenish plates from chloroform; m.p. 126° | Eq. wt., 264.5 Cl, 13.55 | Eq. wt., 263.5 Cl, 13.71 |
| 4. Semicarbazone ... | $C_{14}H_{12}O_3N_3$ | Shaking alcoholic solution with semicarbazide chloride and Na acetate. | Light silky needles; m.p. 279°. | Eq. wt., 303 | Eq. wt., 301.8 |
| 5. Isonitroso derivative ... | $C_{13}H_9O_6N$ | Warming (1) with sodium acetate and sodium nitrite in alcoholic solution; yield, 25%. | Reddish violet need- les; m.p. 212°. | N. 5.09 | N. 5.00 |
| 6. β -4-Acetoxyphe- nyl-gluta- conic acid. | $C_{13}H_{12}O_6$ | Hydrolysis of (1) with dilute NaOH. | Mixed with the synthetical compound in Part I; m.p. 193° with decomp. | | |

Table No. II (Compounds from anisole).

| Name. | Formula. | Method of formation and yield. | Appearance and m.p. or b.p. | Analysis. | |
|---|----------------------|---|--|-------------------------------------|---------------------------------------|
| | | | | Calc. | Found. |
| 1. α -Carboxy- β -4-methoxyphenyl-cyclobutenone. | $C_{12}H_{10}O_4$ | (i) Condensation of anisol with acetone dicarboxylic acid. (ii) Heating the corr. glutaconic acid (a) at its m.p. and (b) with acetyl chloride; yield, 40%. | Yellowish needles from alcohol; m.p. 160°. | Eq. wt., 218 C, 66.05 H, 4.58 | Eq. wt., 217.8 C, 66.12 H, 4.49 |
| 2. Monacetyl derivative of (1). | $C_{14}H_{12}O_5$ | Acetylation of (i) with acetic anhydride; yield, 60%. | Pinkish needles from alcohol; m.p. 118°. | Eq. wt., 260 C, 64.6 H, 4.6 | Eq. wt., 258.5 C, 64.52 H, 4.7 |
| 3. Monochloro derivative of (1). | $C_{12}H_9O_3Cl$ | See table No. I; yield, 55%. | Greenish plates from carbon tetrachloride; m.p. 162°. | Eq. wt., 236.5 Cl, 15.01 | Eq. wt., 237.0 Cl, 14.95 |
| 4. Semicarbazone ... | $C_{13}H_{13}O_4N_3$ | " " yield, 50%. | Short white needles from methyl alcohol; m.p. 213°. | N, 15.27 | N, 15.22 |
| 5. Hydrazone ... | $C_{13}H_{13}O_3N_2$ | " " yield, 90%. | Light leaflets from methyl alcohol; m.p. 188°. | Eq. wt., 308 N, 9.08. | Eq. wt., 307.2 N, 9.14 |
| 6. β -4-Methoxyphenyl glutaconic acid. | $C_{12}H_{12}O_6$ | Hydrolysis of (1) by sodium hydroxide. | Mixed with the synthetical glutaconic acid of Part I m.p. 176° with decomposition. | | |

Table No. III (Compounds from O-cresylmethylether).

| Name. | Formula. | Method of formation and yield. | Appearance and m.p. or b.p. | Analysis. | |
|---|---------------------|---|--|---|--|
| | | | | Calc. | Found. |
| 1. α -Carboxy- β -4-methoxy-3-methyl-phenyl cyclobutenone. | $C_{13}H_{12}O_4$ | Condensation of o-cresyl-methyl ether with acetone dicarboxylic acid; yield 70%. See table No. I for the other 2 methods. | Pale yellow needles from alcohol; m.p. 166°. | Eq. wt., 232 C, 67.24 H, 5.17 | Eq. wt., 231.1 C, 67.2 H, 5.20 |
| 2. Acetyl derivative of (1) ... | $C_{15}H_{14}O_6$ | See Table No. II, yield, 35% | Reddish yellow needles from alcohol; m.p. 137° The barium salt. | Eq. wt., 274 C, 65.7 H, 5.11 Ba, 20.07 | Eq. wt., 273.2 C, 65.6 H, 5.07 Ba, 20.0 |
| 3. Chloroderivative ... | $C_{13}H_{11}O_3Cl$ | See Table No. I, yield, 25% | Yellowish prisms; m.p. 178° with decomp. | Eq. wt., 250.5 Cl, 14.16 | Eq. wt., 249.8 Cl, 14.2 |
| 4. Semicarbazone ... | $C_{14}H_{15}ON_3$ | Yield, 50% | Silky white needles from acetone, m.p. 197°. | Eq. wt., 289 N, 14.53 | Eq. wt., 290.1 N, 14.6 |
| 5. Hydrazone ... | $C_{13}H_{13}ON_2$ | Yield, 60% | Orange leaflets from chloroform m.p. 189°. | Eq. wt., 322 N, 8.7 | Eq. wt., 320.5 N, 8.65 |
| 6. β -4-Methoxy-3-methyl phenyl glutacnic acid. | $C_{13}H_{14}O_6$ | Hydrolysis of (1) with alkali | Mixed with the same acid of Part I, m.p. 172° with decomposition. | | |

The author takes this opportunity to mention his gratitude towards Late Dr. A. N. Meldrum, Ex-Principal of the Royal Institute of Science, Bombay for his advice during the course of this work.

The work is being continued.

THE FOURTH DIMENSION

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Gujarat College.

We are all gradually breaking away from traditions. We do not hold the same views in our social, religious, educational and professional spheres to-day as we held yesterday. The change in our outlook has been rather so rapid that our foundations have been almost shaken and many of us would have started becoming suspicious about the new course of events. One thing is however certain and that is, that even the most conservative of us are trying to understand the advantages of fresh air and ultra-violet rays and at least roam freely in the vast fields of rational thought. Such is the case with us, also, in following the course of Scientific thought during the last three hundred years and particularly during the last thirty years of the present century. The Aristotelian Science and Philosophy remained supreme under the holy sanction of the churches for nearly two thousand years. The first great shock was received from Copernicus ; Galelio, Kepler, followed ; Galelio particularly suffered a good deal of persecution at the hands of the Church Authorities in preaching his new ideas on matter, mass and motion. When Newton came, the times were ripe for an explosion. His Gravitational Theory of Matter which stated that each particle of matter attracted each other particle of matter whether terrestrial or celestial according to the Inverse Square Law was a revolutionary one in the world of Science. The Aristotelian Theory that celestial matter—the matter of which the stars, sun and other planets are composed—was much brighter and superior to the earthly matter, that there was something rhythmical and supernatural in the motions of the celestial bodies was pulled down, as, it could not stand Newton's analysis. After the later stir caused by the Electromagnetic Theory of Maxwell, followed the whole host of fresh theories. The Quantum Theory by Planck, the Theory of Relativity by Einstein, the Theory of the Structure of Atom by Rutherford and later as late as ten years ago, The Theory of Wave mechanics by Heisenburg, Shrodinger and De Broglie. Of all these the Theory of Relativity contributed most towards revolutionising our ideas and the conception of the Fourth Dimension in relation to the universe in which we live became handy to Einstein in illuminating his theory. His theory was tested and retested by experiments and every time it proved successful. We are thus drift-

ting in the world of a *four-dimensional continuum* and each one of us is taking the shortest route in this continuum.

What is the Fourth Dimension? What use is it? The fundamental needs of human nature are its quest after Art and Utility. The conception and the use of the theory of the Fourth Dimension supply both these needs. The theory is an art in itself in the realms of Mathematics and proves its use in abundance in the Relativity Physics. The theory is a beautiful one from the stand-point of a Mathematician and a very useful one from that of a physicist. We shall therefore first treat the theory mathematically and then point out its uses.

Can we imagine a Fourth Dimension? Can a Mathematician himself picture it? We all know what a one dimension is. If a particle is constrained to move on a line which is the simplest instance of one dimension (extension in length only) it requires one co-ordinate to specify its position at any time from the place from which it started viz. its distance from the place. (If a particle is travelling along any curve, its position at any time can also be specified by its actual distance from the point of starting: any curve can thus be regarded as one-dimensional). It requires two co-ordinates to specify the position of a point on a plane (extension in length and breadth) which is the simplest instance of a figure of two dimensions viz. x and y —its distances from two lines which are usually taken perpendicular to each other. A point has position but no extent i.e. is zero-dimensional. Its motion generates one-dimensional line. The one-dimensional line when moved in a direction perpendicular to itself generates a plane which has two dimensions. The two-dimensional plane when moved in a direction perpendicular to itself generates space which is three-dimensional—the space in which we live. In specifying the position of a point in our space, we require three co-ordinates viz. x , y , z its distances from three mutually perpendicular planes, for instance. In any other system of co-ordinates also, three co-ordinates are sufficient to assign completely the position of a point in our space. The co-ordinates x , y , z are analogous to our ideas of length, breadth and height. We are thus able to visualize the position of a point in our space; but, what happens when we try to extend these ideas a step further? Can we imagine a fourth direction not contained within our space and such that it is perpendicular to every line which can be drawn in our space? Can we picture to ourselves the space of our existence moving perpendicular to itself? Neither any person nor a Mathematician can do this but the Mathematician does not stop at his inability of physical perception. He does not even stop to think whether his mathematical extension in the fourth direction which he

does not perceive will have any uses. He only believes in generalizations of his ideas—beautiful extensions of the sphere of his art—irrespective of what uses they may be put to. When the Greek Mathematicians extended the elementary ideas of the Practical Geometry developed by the Egyptians, they did not care to know about its use and the disinterested development of geometry at their hands resulted in Euclid who handed down to us a geometry which is the same now as it was centuries ago when he compiled it. When Descartes in the seventeenth century discovered the co-ordinate Geometry of two dimensions, he merely wanted to solve some problems in which he was interested, irrespective of any use such a geometry would result into. He made the dull life-less equations of Algebra such as for instance $y=x$, $x^2+y^2=25$ speak with eloquence the wonderful properties they possessed. Bodyless phantoms became, as it were, endowed with beautiful bodies. To take only one instance, the Algebraic relation $x^2+y^2=25$ which merely stated that the sum of two squares was equal to twenty-five was according to Descartes visualized as the locus of a point which always moves at a constant distance of five units of length from a fixed point i.e. as a picturesque circle. Any relation between two variables such as $y=f(x)$ fell under the category of some curve and it became possible to study the properties of each species of a curve with an elegance and simplicity never found in geometrical methods alone. Geometry supplied Algebra with imagination, as it were, and Algebra gave Geometry wings. Applications of the analytical methods of Descartes to curves and surfaces in space resulted in the Geometry of three dimensions which further simplified the study of Algebraic relations between the three variables x, y, z , the simplest of them being $x+y+z=k$ and $x^2+y^2+z^2=k^2$ which we now picture to ourselves as a plane and a sphere. If geometrical forms can thus be used with regard to equations involving two and three variables, why can't they be used with regard to equations involving four variables? A plane with two dimensions is required to represent forms involving two variables; a space of three dimensions is required to represent forms involving three variables. A four-dimensional space would thus be required to study algebraic forms involving four variables. It would thus be clear that a fourth dimension arises out of the imagination of a Mathematician as a natural result of his joy in extending his results and generalising them as far as he can.

The Fourth dimension extends vision. A circle when viewed as a one dimensional curve is merely a curved path: when viewed in two dimensions it has a centre and a fixed radius: viewed in three dimensions it is further related to surfaces such as a sphere, a cylinder, a cone etc. Thus the properties of a circle increase in number as

it is viewed in space of higher dimensions. Similarly the properties of any given line or surface will increase in number when investigated in hyperspace. Also, as it requires a three dimensional space to include certain one-dimensional curves (the helix for instance), so in hyper-space hitherto unknown lines and surfaces become mathematically possible. Just as the comprehension of plane geometry is enlarged by viewing plane figures in space, so solid geometry is much illuminated by the geometry of Hyperspace. Hence also the need of the Geometry of the Fourth dimension.

In the Geometry of four-dimensions, four mutually perpendicular lines are taken as the axes of reference, three of which lying in our space, we are able to see. We cannot see how a fourth line can be made perpendicular to the three mutually perpendicular lines at their common point but a mathematician is not stopped at this physical difficulty. He imagines, he can draw such a hypothetical line and deduces the consequences of his hypothesis. Some simple deductions on this hypothesis are given below :—

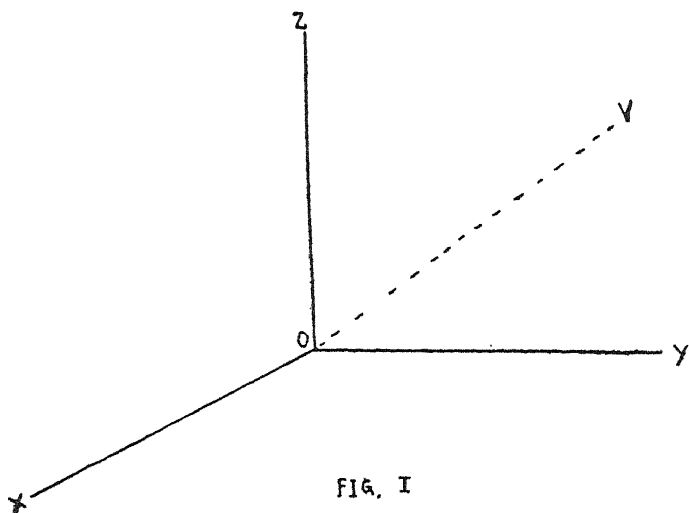


FIG. I

In figure I above, OX , OY , OZ are three mutually perpendicular axes in our space. The invisible OV which is dotted goes out in the fourth direction not contained within our space and is perpendicular to all the lines in our space. Compounded from the four axes in pairs, there are six planes of reference these being XOY , YOZ , ZOX , XOV , YOV , ZOV . These six planes are to be regarded as perpendicular in all the fifteen pairs. Compounded from the four axes in three, there are four flats (three-spaces) of reference these being $OYZV$, $OZVX$, $OVXY$, $OXYZ$. These four three-spaces are to be regarded as perpendicular to each other in all the six pairs. They are also

respectively perpendicular to the four axes OX , OY , OZ , OV . Now OZ and OV are both perpendicular to every line in the plane XOY ; therefore, every line in the plane ZOV is perpendicular to the plane XOY . Planes XOY and ZOV are therefore called absolutely perpendicular. The most that we could see in any three-space of two absolutely perpendicular planes would be one of the planes and a single line of the other e.g. the plane XOY and the line OZ belonging to the plane ZOV . The two planes XOY and ZOV meet at point instead of a line as is the case in three dimensions. In fact two planes which do not lie in the same three-space will not have more than one point in common.

Let us consider what the simplest solid in a space of four dimensions would be. A line unit long moving perpendicular to itself generates a square. The square moving perpendicular to its plane through a unit distance generates a cube. The cube moving perpendicular to its three-space through a unit distance generates a hypercube. We know that the cube has eight corners, twelve edges, and six faces. The hypercube is generated by the motion of the cube through unit distance in the direction of the fourth direction. Thus the hypercube will have sixteen corners, eight of these belonging to the initial position of the cube and eight others to the final position of the cube after it has moved through unit distance in the fourth dimension. It will have thirty-two edges, twenty-four faces, and eight bounding cubes. Each corner of the hypercube is common to four mutually perpendicular edges, to six square faces and to four cubes. Each edge is common to three faces and three cubes and each face is common to two cubes.

In our space, there are only five regular polyhedrons (solids bounded by equal regular polygons) viz., the Tetrahedron, cube, Octahedron, Dodecahedron and Isocahedron; in the space of four dimensions, there would be six regular hypersolids bounded by regular equal polyhedrons. Of these, the first one is bounded by five tetrahedrons, the second by eight cubes, the third by sixteen tetrahedrons, the fourth by twenty-four octahedrons, the fifth by one hundred and twenty dodecahedrons and the sixth by six hundred tetrahedrons. The Hypercube which has been considered above is the simplest of all, as, though it has more bounding solids than the first regular hypersolid, it is right-angled throughout and therefore the standard form for measuring Hyperspace.

The freedom of movement is greater in hyperspace than in our space. In our space, we can have six independent motions—three linear motions (translations) in the directions of the three axes and three rotations about the axes. If we fix three points of a body in

our space, it will prevent all its movement. On the other hand, in the space of four dimensions, there can be four independent translations along the axes and six independent rotations about the six planes of reference. In the hyper-space, if the body is fixed at three points, it can still rotate about the plane containing the three points while at least four of its points must be fixed to prevent all movement. With this greater freedom of movement, things which are not possible for a three-dimensional being become possible for one who is four-dimensional. As we are three-dimensional beings, we have greater freedom of movement than the two-dimensional beings, if any such exist, and the two-dimensional beings, would have greater freedom than the one-dimensional beings (if any). Two dimensional beings would be flat: they would have length and breadth but no height at all. If they have houses, they will consist of walls which are lines and a door will be found by a small break in the line. Their eyes will have one curvature only and the images of objects will fall on a linear sensitive spot. A three-dimensional being can enter the locked room of a two-dimensional being by putting his feet across its walls which have no height i.e. from the direction of the third dimension and play all sorts of pranks such as lifting the hat of the two-dimensional being or stealing away a few of his valuables without breaking through the walls. The two-dimensional being would gape with wonder as to how such extraordinary events could take place. Similarly the three-dimensional beings cannot maintain their privacy before four-dimensional beings, if such exist, even in perfectly closed rooms. We get reports of ghosts entering into closed rooms and surprizing the inmates of the rooms with strange noises and weird cries without being visible. Are ghosts of departed souls, if they exist, four-dimensional? The spiritualists led by Professor Zollner in Gernall thought that the fourth dimension was the abode of the spirit world. Is God who is believed to exist and see in the minutest nooks and corners four-dimensional? Are dreams four-dimensional? Is this the reason of a number of events being viewed in a moment in the dreams? Has ether which possesses so many contradictory properties anything to do with the fourth dimension?

The question of symmetry is a fascinating one.



FIG. II

In figure II below lines AB and $A'B'$ are symmetrical about the point O and are lying on an extended one-dimensional line. It will not be possible for us to make A coincide with A' and B with B' by *any* motion along the line but when AB is rotated through 180° in the two-dimensional plane of the paper and moved so that A coincides with A' and B with B' , this will be possible.

In figure III below, the two triangles ABC and $A'B'C'$ are symmetrical with respect to the line XY in the plane of the paper. The triangle ABC cannot be made to coincide with the triangle $A'B'C'$ by any movement in the plane whatever but it will have first to be turned upside down in the space of three dimensions and moved to coincide with $A'B'C'$ i.e. a rotation of the triangle ABC through 180° in the space of three dimensions is necessary before it can be made to coincide with $A'B'C'$.

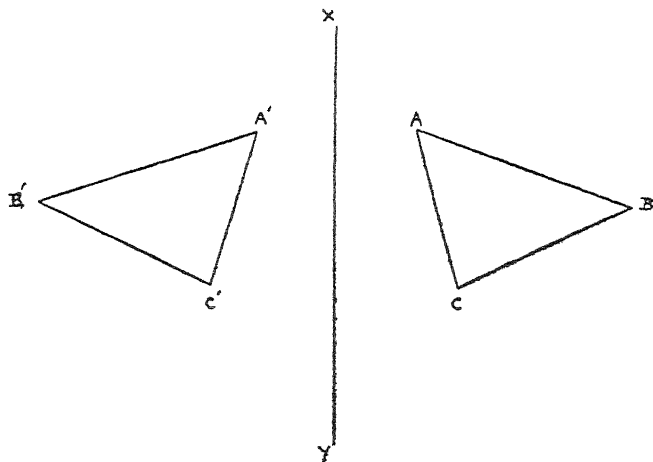


FIG. III

Similarly two figures which are symmetrical with respect to a plane in three-dimensional space can be made to coincide with each other if one of them is taken in the fourth dimension, rotated there through 180° and then placed on the other. The operation of making two symmetrical figures coincide has to be, therefore, always made in a higher dimension. A right glove, turned over through the space of four dimensions becomes a left glove; a right shoe becomes left shoe. A right-handed man becomes a left-handed man. He does not use a different hand after his rotation through 180° in the fourth dimension, but the hand which he then uses appears to everybody else as his left hand. In fact, his point of view is changed so that every body else appears to him changed also. Letters appear to him turned backwards as in the Printing Press, the hands of a clock go

backward and the whole world appears to him as a looking-glass world.

We do not know whether there is a four-dimensional space but on the hypothesis of its existence, we have so far deduced some of the interesting consequences. A Mathematician can build up as many geometries as he likes : only these will depend on the hypotheses with which he starts. His development of the two Non-Euclidean Geometries known by their titles—Hyperbolic Geometry and Elliptic Geometry—shows us that he does not care so much for the use of those Geometries as for the logic of the system he pursues and for the extension of thought in unexplored fields. There are certain statements in Geometry which are considered as Axioms ; these are supposed to be self-evident truths and do not require any proof. There are other statements which are known as postulates which may not be self-evident but which cannot be proved by any simpler proposition. One of the postulates of Euclid runs as follows : “ If a straight line falling on two straight lines make the sum of the interior angles on the same side less than two right angles, the two straight lines, if produced indefinitely, meet on that side on which are the angles less than two right angles.” Many geometers tried to demonstrate its truth. Great ingenuity was expended but no advance was made till modern research vindicated Euclid and justified his decision in assigning his great proposition a place amongst the independent assumptions necessary for the development of Euclidean Geometry as a logical system. Since the truth of the parallel postulate cannot be demonstrated by any simpler axiom, both Lobachevsky in Russia and Bolyai in Hungary denied it as true and independently worked out a system of Geometry on the hypothesis that two lines can be drawn through a point parallel to a given line. The Geometry of both of them is as logical and consistent as that of Euclid's and is known as Hyperbolic Geometry. Riemann further argued that yet another self-consistent Geometry could be built up on the hypothesis that no straight line could be drawn through a given point parallel to a given line. This Geometry was called Elliptic Geometry. The two non-Euclidean geometries were logically as consistent as Euclid's but were considered to be inconsistent with reality until a space was known for which they were found to be true. It was found that Riemann's geometry was none other than that of the spherical surface (a two-dimensional surface of constant positive curvature) provided arcs of great circles are taken as geodetic lines. In 1868, the Italian Beltrami discovered a surface for which Lobachevski's Geometry held true—the so called pseudo-spherical surface of infinite extent (a two-dimensional space of constant negative curvature).

Riemann also showed that there are logically also three kinds of space of three dimensions, with properties analogous to the two-dimensional spaces mentioned. They are distinguished by the so-called measure of space curvature (purely analytical, not denoting curvature for sense-perception). If this constant is zero, we have Euclidean space; if positive, spherical space; and, if negative, a pseudo-spherical space.

A Mathematician can thus, logically build up as many geometries as the hypotheses with which he starts and we make use of that particular geometry which fits in with our experience and conditions of our existence. What is the use of the Geometry of the Fourth Dimension? It has been so far customary to describe the three-space in which we live as flat, uncurved space. This description is tacitly assumed on the ground that the linear property is obvious and is approximately correct so far as observations within normal distances go. Now, the Theory of relativity has been established beyond doubt and mathematical calculations involved in the theory show that on a grand scale in which large stellar distances are considered, the space of our universe is not uncurved. The very notion of curvature for a curve or a surface or a region implies some uncurved configuration by reference to which the curvature can be defined and estimated. Thus, the curvature at any point of a curve, which exists in the Euclidean space of two or three dimensions is a mathematical measure of the deviation of the curve from straightness, the measure being framed by reference to successive straight lines in the two-dimensional or three-dimensional space in which the curve lies. Also, the curvature at any point of a surface is estimated with reference to its organic geodetic curves: and all these curvatures are estimated by reference to deviations from straight lines in the Euclidean three-space containing the two-dimensional surface. It would be thus clear that the important conception is, that in framing a mathematical measure of curvature of any curved configuration, we require an uncurved space more extensive in dimension than the curved configuration in question. If, therefore, as the Theory of Relativity shows, the space of our universe is a curved one, the mathematical conception of the curvature of such a space would require the existence of some further space of ultimate reference characterised by complete linearity. Thus has arisen the demand for at least one more dimension, additional to the three dimensions possessed by our space. Hence the use of the Geometry of four dimensions.

Also, time as a co-ordinate is gradually assuming an independent position of a fourth dimension although in a different sense from the usual one attached to the word dimension. Nothing lives at no time

or no-where. For a complete specification of an object, its location in space and time simultaneously is necessary. Consider, for instance, our material bodies. We are conscious of a gradual change of shape and position of all its parts and yet at the same time, we are conscious of a continuing identity throughout all these changes. Our past experiences are as real as the experiences we are now undergoing. Those past experiences or phases of our existence are as much a part of us as the present ones and yet owing to the limitations of our senses, we can reproduce past conditions only in memory. Nevertheless, our lives in their completeness are made up of the sum total of our experiences and if our whole lives are considered as units and each period of which we are conscious requires a three-dimensional space, then each individual may be regarded as a four-dimensional solid.

When Einstein announced his Theory of Relativity, he said that observers in different relative motion would make different observations on the same event. The events which would for instance be recorded as simultaneous by an observer on Earth would not be simultaneous for an observer on Mars; on the other hand events which take place at different times on Earth may be seen as simultaneous by an observer on Mars. Again, the distance between any two bodies measured by observers on Earth and Mars will not be the same. Einstein asserts that the length and time-lapse are relative conceptions. They vary with the state of motion of an observer. A man carries, as it were, his own particular space and time about with him. The behaviour of his instruments, the measuring rods and clocks varies with his motion. There is no experiment whatever which will show the observer whether he is absolutely at rest.

Each observer carries his own space and time about with him but though they vary in their measurements of length and time, they all invariably arrive at the same figure for the velocity of light viz, 186000 miles per second. Also, if any given observer takes his space and time measurements on a pair of events and combines them in a certain way, he will get a certain result. If another observer combines his measurements for the same pair of events in the same way he will get the same result. The precise technique by which the measurements are combined is of no importance to our argument. The important fact is, that there exists a relation between any pair of events which is the same for all observers. This relation, it is obvious, is more fundamental than either space or time taken separately. It refers to something which does not vary with the state of the observer. What is this something?

The correct interpretation of the fact that there is an invariant relation between any two events is given by Minkowski. He showed

that this relation (which is called the interval) was, in its mathematical expression, analogous to the mathematical expression for a distance. He suggested, therefore, that the interval is a distance of some kind. But if the interval is to be regarded as a distance, it must be regarded as such in a *four-dimensional continuum*. Minkowski did not hesitate to take this step. The actual universe in which events exist is, he asserted, a four-dimensional universe. Our minds split up this universe into three dimensions of space and one dimension of time. Different observers, as we have seen, split up the universe differently. They take different cross-sections, as it were, of the four-dimensional reality ; therefore, they have different space and time measurements. Only those quantities which refer to the four-dimensional reality itself are the same for all observers. Of such quantities the interval is one.

The fact that the interval could be regarded as a distance in a four-dimensional continuum immediately illuminated the whole Theory of Relativity and showed it in more relief. It showed that the geometry which must be applied to the universe was not as had been supposed Euclidean Geometry. The formula for the interval, if interpreted as a distance, made it clear that the geometry of the four-dimensional continuum was not Euclidean. It can be deduced, for instance, that in a continuum subject to this geometry, there is a maximum velocity. In a Euclidean continuum (our space of three dimensions regarded as flat), it is theoretically possible for an infinite velocity to exist. Whatever speed the particle is travelling at, we can always imagine it travelling at a greater speed. But in a continuum, governed by the geometry of four dimensions called semi-Euclidean, this is not the case. An infinite velocity is not possible in such a continuum. The ultimate velocity is a certain finite velocity viz., the velocity of light. It is therefore strongly confirmatory of Minkowski's conception of the universe as a four-dimensional continuum that the velocity of light is found in the Relativity Theory to play the part of an ultimate velocity. The velocity of a material body cannot, according to the Theory of Relativity, ever exceed the velocity of light ; for it can be shewn that the mass of a body increases with its velocity and increases in such a way that at the velocity of light, it is infinite. This can only mean that the speed of light is a natural limit of moving matter.

The Theory of the four-dimensional continuum has been thus proved very helpful to the Theory of Relativity, which has been tested and retested and generally acknowledged as true. It would be, therefore, so far true to say that physically all of us are born, brought up and move in our courses in a four-dimensional continuum. The

Fourth Dimension has been, mathematically, an artistic phantom of a mathematician's imagination but physically it has turned out to be the fruitful union of time with space in a four-dimensional continuum.

The four-dimensional Geometry can be and has been, in fact further extended by writers such as Cayley, Grassmann, Riemann and the Italian Geometer Veronese. The Physicist makes use of this geometry in picturing the atom which escapes being photographed every time the lens of his experimental methods is held towards it. The Theory of the Atom was first found seriously insufficient in 1925 and since that time, an entirely different picture has been developed by Heisenberg, Shrodinger, De Broglie etc. This Theory is however entirely mathematical.

The electron, for instance, on this theory is described not as a particle but as a system of waves. These waves are located within what is called "Configuration Space". This configuration space is certainly not ordinary physical space for the reason that each electron requires a three-dimensional configuration space to itself. Thus two electrons require a space of six dimensions in which to exist, three electrons a nine-dimensional space etc.

A modest attempt has been made in the above lines to show that the strange conception of the fourth Dimension has been found both picturesque and useful. If the attempt has also served the purpose which it was also meant to serve, of elucidating the ideas underlying the conception to a non-mathematical reader of the journal, the writer would feel content.

THE TEACHING OF GEOMETRICAL OPTICS

BY

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In the year 1929, the Physical Society of London held a general discussion on the teaching of geometrical optics. Following this, a committee was appointed to examine and report on the whole question. The report was published last year.* The committee was widely representative of physicists engaged in industry, teaching, and research, including members of great eminence, so that the report must necessarily carry great weight. It is therefore opportune to draw the attention of physics teachers to the problems discussed in this report, and to the recommendations made.

The investigation showed (as, indeed, most physics teachers knew) that there exist great divergencies in the methods employed in the teaching of geometrical optics, particularly in its elementary stages; and that the methods employed by practical opticians differ from those generally used by teachers. The committee were strongly of the opinion that more uniformity is desirable, especially in regard to standard definitions and conventions of signs. Text-books differ widely amongst themselves, to the confusion of the student who is energetic enough to consult more than one; and furthermore, a student who subsequently enters the optical industry has generally to learn a new system of conventions and change his whole approach to the subject.

Certain recommendations are strong and unanimous, such, for example, as that the sign convention for the focal lengths of lenses and mirrors, universally employed amongst practical opticians, should be adopted by teachers also. Thus a converging system (a concave mirror or a convex lens), is positive, and a positive sign is attached to its focal length. Conversely, a diverging system (a convex mirror or a concave lens) is negative, and has a negative focal length.

In the optical industry, however, a lens is generally specified by its power rather than by its focal length. This should also be done by physics teachers, who at present very often work exclusively with focal lengths. It is almost unnecessary to point out how this simplifies

* Report on the Teaching of Geometrical Optics: Physical Society: 1934.

the calculations. Thus, for two thin lenses in contact, the equation

$$F_1 + F_2 = F$$

gives the properties of the combination much more simply than

$$1/f_1 + 1/f_2 = 1/f.$$

The power should have the same sign as the focal length. The magnitude of the power, for a lens or mirror, is the reciprocal of the focal length in metres. Conversely, the focal length is the reciprocal of the power expressed in dioptries. The definition of power for a more complex optical system, such as a telescope, is considered in the report, and the following standard definitions are recommended :

- (a) A reflecting or refracting instrument is said to be of zero power if the image it forms of an infinitely distant object is at an infinite distance from the instrument.
- (b) Axially symmetrical instruments not of zero power are either of positive or negative power. An instrument is said to be of positive power if it produces an inverted image of an infinitely distant object, and of negative power if it produces an upright image of an infinitely distant object.
- (c) The numerical value of the power of the instrument (measured in dioptries) is the small angle (measured in radians) subtended by an infinitely distant object, divided by the length (measured in metres) of its image.

In these definitions, it is evident that every word has been carefully weighed. It would be advisable to adopt them generally, but they would clearly not usually be given to students in the earliest stages. We have not space to discuss them in detail, however, and we pass on to the question of conventions of signs.

We may assign positive and negative signs to the distances of object and image from the reflecting or refracting surface according to a variety of schemes. The most common way is to treat these distances (s and s') as measurements made along the axis of symmetry of the instrument, so that the whole consideration is restricted to rays whose paths are near the axis. There are then five possible ways of allocating signs, denoted by group I. These are :

- (1) The positive direction is the initial direction of progress of the light. (e. g. Robertson : " Introduction to Physical Optics ")
- (2) The negative direction is the initial direction of progress of the light. (e. g. Watson : " Text book of Physics ")
- (3) s and s' are positive when measured in opposite directions, the positive direction of s' being the positive direction of case (1). (e. g. Drude's " Theory of Optics ")

(4) As above, but the positive direction of s is that of case (1). (No books are known to use this convention)

(5) The signs are based on the Cartesian framework, and are independent of the direction of the light. (e.g. Houston: "Treatise on Light")

There is a further group of systems (group II) in which the conventions are of a different kind. The distances are measured, not along the axis, but actually along the path of the rays, so that we can obtain exact equations, even when the angles are no longer small. Four cases are possible, but only the following (case (1)) need be considered in practice. Positive signs are given to s and s' when they represent real rays, i.e., distances over which the light actually travels. Negative signs are given to distances over which the light does not actually travel, i.e., virtual rays. The convention is thus independent both of the Cartesian system, and of the direction of progress of the light.

The report recommends that for general purposes either the system of group I, case (1); or that of group II, case (1) should be adopted. They consider that the time has not come when it will be practicable to recommend the exclusive use of one convention, although, from many points of view, this would be desirable.

In considering the recommendations which have been outlined, we are concerned chiefly with the teaching of geometrical optics in its elementary stages. For the degree work, the student should have reached a stage where conventions of sign are of less importance. But for a stage of instruction represented, say, by the Intermediate examination of this University, it would appear that the second system recommended had great advantages, although at present it is very little used by teachers.

Firstly, the distinction between positive and negative distances has a physical significance which is easily appreciated by the student. Either the light does, or does not, traverse the path considered. No confusion can arise by turning the apparatus round, as in some of the Cartesian systems which involve the direction of progress of the light.

Secondly, it is just as simple to deduce the exact as the approximate equations, for as measurements are made along the rays one is not limited to paraxial rays. Any approximation introduced by assuming the angles to be small is made at the end of the calculation, not at the beginning. This gives a greater sense of reality to the whole procedure.

Thirdly, the system leads on to more advanced work, and to practical lens computing, as readily as any of the more customary conventions.

Fourthly, the system gives the same equation for mirrors and lenses, whereas the Cartesian systems give different equations. The equation is furthermore the simplest possible, namely :

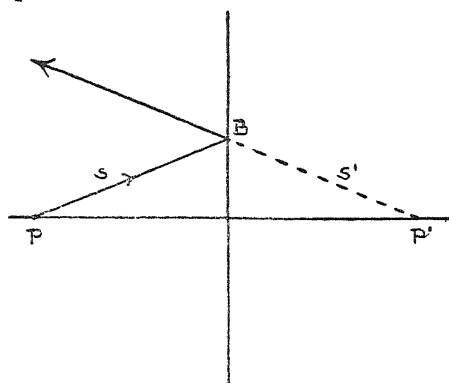
$$1/s + 1/s' = F$$

Finally, to illustrate the system, we may show how the standard imagery relation may be deduced in some simple cases. The law of refraction will be expressed in the form

$$n \sin \phi = n' \sin \phi'$$

It is highly desirable, in teaching, to present the law in this symmetrical form from the very beginning.

Reflection at a plane mirror



(Figure 1)

From the geometry of the figure

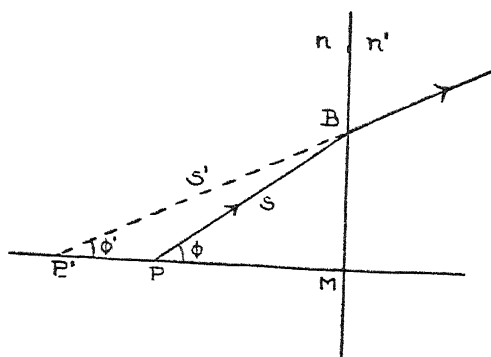
$$PB = P'B$$

$$\text{But } PB = s, P'B = -s'$$

$$\text{Hence } s + s' = 0 \text{ or, dividing by } ss'$$

$$1/s + 1/s' = 0$$

Refraction at a plane surface



(Figure 2)

From the geometry of the figure

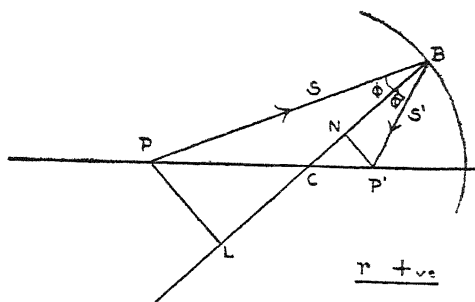
$$BM = PB \sin \phi = P'B \sin \phi'$$

But $PB = s$; $P'B = -s'$; $n \sin \phi = n' \sin \phi'$

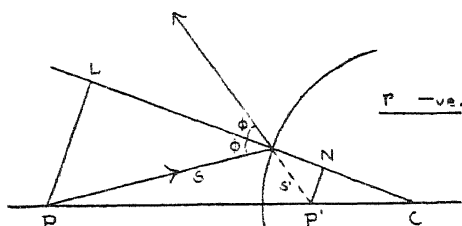
Hence $n's + ns' = 0$ or, dividing by ss'

$$n/s + n'/s' = 0$$

Reflection at a spherical mirror



(Figure 3)



(Figure 4)

Construction:—draw perpendiculars to the normal from the object and image points.

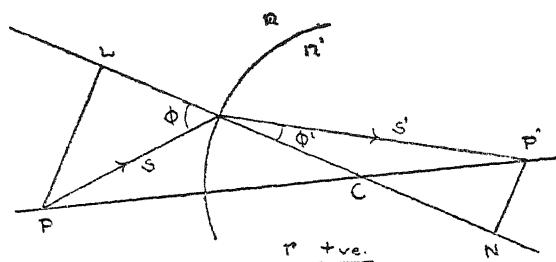
$$\text{Then } CL/PL = CN/NP'$$

$$\text{Or } (s \cos \phi - r)/s \sin \phi = (r - s' \cos \phi)/s' \sin \phi$$

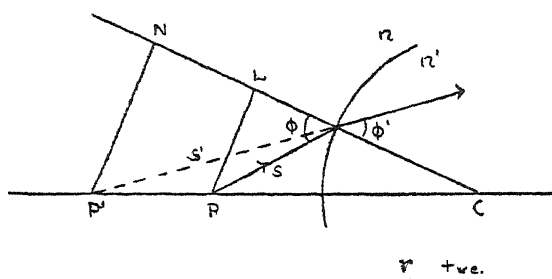
$$\text{Hence } 1/s + 1/s' = 2 \cos \phi / r = F$$

This is the exact equation: for paraxial rays we may now set $\cos \phi = 1$.

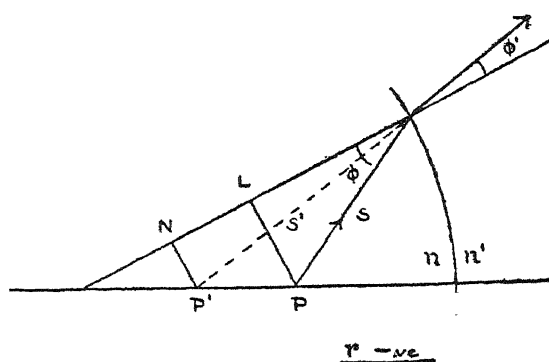
It will be seen that this derivation applies to both (indeed to all possible) figures.

Refraction at a spherical surface

(Figure 5)



(Figure 6)



(Figure 7)

Draw perpendiculars as before ;

then $CL/PL = CN/NP'$

or $(s \cos \phi + r)/s \sin \phi = (s' \cos \phi' - r)/s' \sin \phi'$

Hence $n/s + n'/s' = (n' \cos \phi' - n \cos \phi)/r = F$

Here again, we may set $\cos \phi = 1 = \cos \phi'$ for paraxial rays.

Refraction through a thin lens

Consider the two refractions separately. The first surface, if acting alone, would produce an image, which we may regard as the object for the second refraction. If this first image were real, it would lie beyond the lens and be equivalent to a virtual object for the second refraction. Conversely, if it were virtual, it would lie in front of the lens and be equivalent to a real object for the second refraction. Thus in either case, if s' be the image distance for the first refraction, $-s'$ is the object distance for the second refraction. Thus, if the final image distance after both refractions be s'' , we shall have

$$n/s + n'/s' = F_1 \text{ for the first refraction}$$

$$-n'/s' + n''/s'' = F_2 \text{ for the second refraction}$$

(The refractive indices for the first refraction are n & n' , for the second, n' & n'')

$$\text{Adding the equations, } n/s + n''/s'' = F_1 + F_2 = F$$

If the lens has air on both sides, we may write $n = n'' = 1$.

$$\text{Hence } 1/s + 1/s'' = F$$

Naturally the accuracy of this equation is limited by the condition we have imposed that the lens be thin. It is not difficult to develop exact equations for a thick lens.

Conjugate foci

We now see that the equation $1/s + 1/s'$ applies without change to mirrors and lenses, whether convex or concave. It is very simple to calculate a series of conjugate foci for all cases. Indeed the following table, where corresponding values are in the same columns, may be written down at once:

| | | | | | | | | | |
|--------|-----------|-------|----------|-------|-----------|--------|-------|--------|-----------|
| s | $+\infty$ | $2f$ | f | $f/2$ | $+O$ | $-f/2$ | $-f$ | $-2f$ | $-\infty$ |
| $1/s$ | $+O$ | $F/2$ | F | $2F$ | $+\infty$ | $-2F$ | $-F$ | $-F/2$ | $-O$ |
| $1/s'$ | F | $F/2$ | O | $-F$ | $-\infty$ | $3F$ | $2F$ | $3F/2$ | F |
| s' | f | $2f$ | ∞ | $-f$ | $-O$ | $f/3$ | $f/2$ | $2f/3$ | f |

It is a useful exercise for the student to plot on a graph the corresponding values of s and s' , for various cases of mirrors and lenses, by giving F a series of positive and negative values,

There are, of course, other forms of the object-image equation, in which the measurements may be referred to the foci, or to the nodes, instead of to the surfaces. These other forms are quite easily introduced. The system also lends itself to calculating the formulæ for the longitudinal and transverse magnifications. Without going into such matters, enough has been said to demonstrate the simplicity and directness of the sign conventions which have been proposed.

It is to be hoped that physics teachers in the University generally will not ignore such a weighty contribution to the pedagogy of the subject as is represented by the Physical Society's report. We are at present, perhaps, far too dependent on text-books both for matter and method in Physics teaching. In Wilson College the conventions recommended are already being tried for elementary teaching. Only experience can show whether the arguments here advanced are sound. The sooner that experience is gained, the better.

TECHNIQUE OF THE FAR INFRA-RED INVESTIGATIONS.

Dr. N. R. TAWDE, Y. G. NAIK AND D. D. DESAI,

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Historical

Of recent years, the study of the spectral region known as the "far" and "near" infra-red has proved of much value in the investigation of molecular structure. No doubt the structure of a large number of compounds has of late been elucidated by newer methods of Raman spectra, yet substances not easily accessible to this procedure have to be attempted by infra-red methods. On account of the experimental difficulties involved in this kind of work, relatively few attempts are made to investigate the infra-red region. The infra-red, for purposes of experiment, falls into two divisions. The first which is called the near infra-red extends from $1\ \mu$ to $23\ \mu$, ($1\ \mu = 10^{-4}$ cms.) and the 2nd called 'far' infra-red covers region from $23\ \mu$ and onwards. This latter which generally gives a clue to problems of free rotation in a molecule has not been studied in so great a detail as the 'near' infra-red which covers vibration frequencies of a molecule superposed over its rotation frequencies. The near infra-red is more accessible to experiment because substances transparent to these radiations and ready-made prism spectrometers are easily available.

The experimental technique of the far infra-red is relatively very difficult on account of the lack of suitable material transparent to this region. The dispersion in this region is best achieved by means of a reflection or a wire-grating. Measurements with the help of wire-gratings, have been carried out in recent years by various investigators. The work of Rubens¹ in this connection in 1921, stands the foremost. Witt² was the next to use this type of apparatus successfully. Czerny's³ work on the study of rotation spectrum of HCl & Halogen derivatives in the far infra-red was a further milestone in the progress of these investigations. Leiss⁴ developed a refined apparatus using wire-grating. Barnes⁵ made many improvements in the existing technique of using wire-grating for this work.

INTRODUCTION

With a view to study the far infra-red region, the authors have been engaged for some time in setting up a wire-grating apparatus. During the course of the work, we have consulted all the available literature on the subject and have made use of it in setting up of the

present apparatus with slight modifications where necessary. It is therefore thought desirable to put on record a coherent and connected account of the work of various authors which has come within our reach and which has direct bearing on purely experimental aspect of the subject of far infra-red absorption spectra. This, in the light of experience gained by us, might serve as a compact reference guide to workers engaged in this field.

EXPERIMENTAL.

The most essential factors in the apparatus for the far infra-red measurements are (1) the source of continuous radiation, (2) the dispersing system, and (3) the detecting instruments.

These are shown in the following diagrammatic sketch.

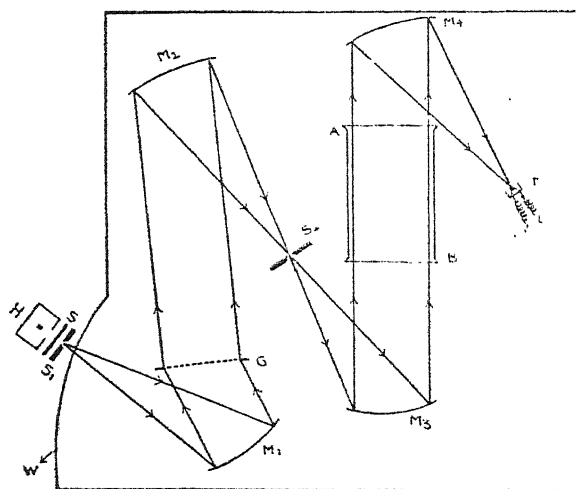


Fig. 1

Article 3: Technique of the Far Infra-Red Investigations by Dr. N. R. Tawde
Y. G. Naik and D. D. Desai.

H Globar Heater

S Shutter for cutting off the radiation

S₁ and S₂ Slits

W Celluloid Window

M₁, M₂, M₃ and M₄ Stainless Steel Mirrors.

G Wire-grating

A B Absorption Tube

T Thermopile with leads going to Galvanometer

For systematic treatment the subject is divided and explained under the following heads :

(1) Source of radiation.

- (2) Collimation of light.
- (3) Dispersion system (wire-grating) with special reference to the purity of spectra.
- (4) Slits.
- (5) Absorption Cells.
- (6) Apparatus for detecting the radiation.
- (7) Assemblage of the whole apparatus.

(1) SOURCE OF RADIATION.

Among the sources that give out appreciable radiation in the far infra-red may be mentioned the Welbach mantle, the Nernst filament and the globar heaters. Trials were given to each of these and ultimately it was found that globar heaters serve the purpose well. The Welbach mantle was found to have low energy of emission, and was liable to fluctuations owing to variation of gas pressure. Platinum coated with mantle foils and heated electrically was next tried but it did not serve the purpose better. Both these sources gave very weak radiations in the far infra-red and were undetectable by our instruments.

The Nernst filament which was next attempted was more efficient than the mantle lamp. As it takes a small current of 0.8 amp., a small variation in the strength of the current brings about a large alteration in the total energy of emission. The light transmitted through slit S_1 is also likely to suffer changes in magnitude and direction, as the thin filament has a tendency to bend at higher temperatures. Though the life-period of the filament is generally supposed to be of the order of 250 hours, it is liable to be damaged any time by a slight excess of current or by a sudden stoppage of it.

Finally we secured Globar heaters through the courtesy of the B. E. S. T. Company and have found them to be very satisfactory for our purpose. Globar heaters have been successfully used by—Rawlins and Taylor⁶ and by Strong⁷. The heating element is held between two special terminals provided with spring arrangement in one of them, to make allowance for expansion due to heat. The original heater required a large current and was therefore reduced in cross-section sufficient to attain brightness with a current of about 10 amps. This heater was found to possess the following advantage over the Nernst filament: (1) it does not require pre-heating; (2) its area of emission is greater which allows use of slits with large aperture; (3) it can be used without damage for an appreciable period; and (4) small fluctuations in a current strength of 10 amps. do not bring about a great change in the total energy emitted.

2. COLLIMATION OF LIGHT.

It should be remembered that for collimation of radiation, devices involving the use of most of the materials transparent to visible and near infra-red are out of consideration. The collimation of light has therefore to be effected by means of metallic mirrors made of stainless steel as it is found that they reflect more than 99% of the incident radiation. The mirrors M_2 , M_3 , M_4 , shown in the figure 1 are of 8 cms. diameter and 45 cms. focal length. The Mirror M_1 , is however of a large diameter of 16 cms. and the same focal length as above. This latter requires to be so, for the reason that when it is rotated, the whole grating surface should remain illuminated. Barker and Meyer⁸ have particularly laid stress on this point. The mirrors have fine independent screw movements for rotation about vertical and horizontal axis, which have been effected by the Junior Lab. Workshop, Poona, on specially prepared stands. Heavy loading at the base allows for their stability. The heater, the mirrors, grating and the thermopile have to be adjusted with their centres in the same horizontal plane. Astigmatism has been minimized after the manner shown by Czerny & Turner.⁹ The inclinations of mirrors with each other have to be as small as possible. The mirror M_1 rotates along with the heater so that angle, through which it rotates is the same as the angle through which the diffracted beam is deflected. The rotation of M_1 is necessary to select a particular band of the spectrum, which is brought into focus at slit S_2 . The rotating system ought to be able to turn without causing any mechanical disturbance to the other stable components. This, however, is not achieved in practice and so we propose to follow the arrangement of Barnes⁹, wherein he selects a particular band by the rotation of a single plane mirror placed behind the grating, the heater as well as mirror M_1 remaining fixed. The present arrangement is shown in fig. II.

3. DISPERSION SYSTEM.

This consists of a wire-grating, got specially prepared from the Laboratory of Prof. M. N. Saha, Allahabad. In its size of $2'' \times 1.5''$, the number of wires were 204 and its average grating constant was $\cdot 02515$ cms. This grating is capable of working upto the region 250μ . The angle of diffraction for the region 23μ to 250μ lies between 5° and 84° . The grating is also mounted on a stand and is capable of rotation about the vertical and horizontal axis. Grating is placed as near to the mirror M_1 as possible so that even for the large deflections of the mirror M_1 it remains completely illuminated. The position of the grating was so adjusted that the deflections of the galvanometer, when the mirror M_1 turned through equal angles from the zero position on either side of the grating, were equal. The Zero position of the

mirror was taken as that one, for which galvanometer gave the maximum deflection.

Purity of Spectra: There is always a chance of higher order spectra of the near infra-red overlapping the spectrum of far infra-red. It has been observed by Czerny³ and Barnes⁵ that a small % of the energy of 20μ , occurring as an impurity could easily produce a deflection of the same order as that produced by the total energy at 100μ in the first order. For this reason, the third order of 33μ and fifth order of 20μ at 100μ are dangerous. It is therefore necessary to eliminate the second and higher order spectra. The thickness of the wire is very approximately equal to half the grating constant so that the even order spectra were automatically eliminated. In order to see whether second and all even order spectra were really missing, yellow line of sodium was examined by means of the grating and it was found that the grating gave only odd order spectra. Owing to imperfection in the grating, however, traces of even orders of the near infra-red may be present. In order to eliminate these along with 3rd and higher orders of the near infra-red, various devices have been used by different workers, such as, Barker, Mayer, Sleater, Czerny and Barnes. Czerny uses soot deposited on paraffin to cut off the near infra-red. Barnes has made a series of experiments on the power of transmission of films of various types and finds that celluloid film having thickness 1μ and coated with deposit of camphor soot is quite good. It has about 80% transmission for wave lengths above 30μ . Barnes also gives a list of substances effective in giving restrahlen rays for a particular band of the spectrum. They are :—

| | | |
|-------------------|------|-------------------------|
| Ca F ₂ | from | 20 μ to 30 μ . |
| Aragonite | from | 30 μ to 40 μ . |
| NaCl | „ | 45 μ to 55 μ |
| KCl | „ | 55 μ to 70 μ . |
| KBr. | from | 70 μ to 94 μ . |
| TiCl | „ | 94 μ to 134 μ . |

We propose to use flourspar plate which absorbs all the far infra-red. The plate when brought into the path of rays will allow only the near infra-red and the deflections obtained will be eliminated from another set of readings taken without the plate. This procedure will enable deflection to be noted only for the far-infra-red.

4. SLITS (Fig. 1)

The slit s_1 (Fig. 1) serves as the object and s_2 is placed in order that only a particular diffracted beam will pass through it. The height of each of the slit openings was 3 cms. and preliminary observations have been taken with a slit width of 1.5 mms. In practice

however, it has been found necessary to work with various slit openings, to compensate for the weakening of intensity in the long wavelength regions. Barnes⁵ has given the following suitable slit widths for various portions of spectrum.

| Regions. | Slitwidth. |
|--------------------------|------------|
| 30 μ to 85 μ | 0.75 mm. |
| 85 μ to 122 μ | 1.25 mms., |
| 122 μ to 180 μ . | 2.0 mms. |

Large slit widths are objectionable on the ground that they reduce the resolution of bands. But the resolution is to be sacrificed here in order to enable measuring instruments to detect the radiation in the spectrum.

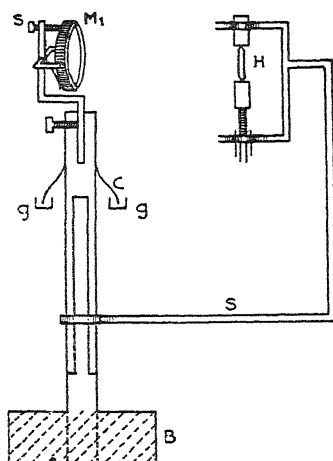


Fig. II

Fig. II.

Article 3; Technique of the Far-Infra-Red Investigations by
Dr. N. R. Tawde Y. G. Naik and D. D. Desai.

(Figure 2).

Figure 2.

- S Screw for tilting the mirror about horizontal axis.
- M Stainless Steel Mirror.
- C Metal Cup.
- g, g. Groove containing mercury.
- S Shaft attached to the rotating pillar.
- B Cement Base for the pillar.
- H Globar Heater.

5. ABSORPTION TUBES.

The tubes are made of brass about 6" long and 3" in diameter. They are provided with stopcocks to allow gases to be filled in. The end openings are sealed with windows of transparent material. This

material should be of a very small absorption coefficient. Great difficulty is generally experienced in getting a suitable substance. Mica, quartz, cellulose, paraffin and Zapon lack films are among the materials that are found transparent to far infra-red radiation to various degrees, and have been used by different workers. We used paraffin and cellulose for preparing window films. Czerny³ and Kellner¹⁰ prepared films by spreading paraffin upon surface of glass covered with celluloid film and also on water surface. But they possess certain disadvantages as was found by Czerny and verified by us.

For achieving a better film in point of thickness and uniformity and some other factors, a film prepared upon mercury surface has been shown by us to be more efficient as reported in a recent communication.¹¹

For accurate and rapid measurements, two tubes are used with great advantage. Some radiation is necessarily lost by absorption through the windows and this has to be accounted for before proceeding with the measurements on the required substance. It is rather an inconvenient procedure to take an initial measurement with an empty tube and then another with the same tube filled. To avoid this, two tubes fixed with similar windows are mounted parallel to each other on a rotating wheel and by external contrivance, each one is brought in succession in the path of beam. This arrangement has been illustrated in Fig. 3.

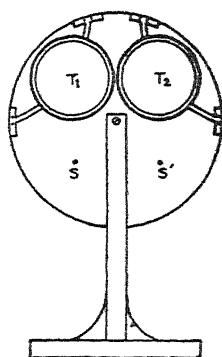


Fig. III

Fig. III.

Article 3 ; Technique of the Far Infra-Red Investigations, by
Dr. N. R. Tawde, Y. G. Naik and D. D. Desai.
(Figure 3).

T_1 and T_2 Absorption Tubes.

S and S' Stops for keeping the absorption tube in position.

6. APPARATUS FOR DETECTING THE RADIATION.

The Moll linear thermopile having 30 elements in a row is being used in conjunction with Pye moving-coil galvanometer for measuring the spectrum. It has been found fairly sensitive to weak radiations. Mounted on a bracket in a wall and separated from the thermopile by a distance of about 5 meters, the galvanometer was given sufficient immunity from mechanical disturbance by means of glass-paper packing below its base. In spite of these precautions the initial zero of deflection was found to be fluctuating for some reasons. The cause was traced to two factors. One was the adiabatic changes within the air space of the thermopile and the other due to heating of galvanometer junctions by the radiations from the slit illuminating its mirror. These were eliminated by enclosing the galvanometer completely in a cardboard box, leaving only a glass window for the beam of light. In the case of the thermopile, its opening was covered by a very thin film of paraffin. These precautions were found sufficient to maintain the zero of the galvanometer constant even during day-time.

7. ASSEMBLAGE OF THE WHOLE APPARATUS.

All the component parts (except the heater) shown in Fig. 1 were placed on a table (100×100 cms.) in their relative mapped positions. An enclosure was made for the whole top of the table in the form of a closed wooden box which had also to be made free from water-vapour and CO_2 before it could be used for any measurement. Precise arrangements were made to operate and observe by one person the rotation of mirror M_1 , the shutters and the absorption tubes, and to observe at the same time the galvanometer deflection. To avoid outside mechanical disturbances due to traffic and busy surroundings in the vicinity, readings are generally taken during night. The heater is switched on about $1\frac{1}{2}$ hours earlier so that only when all conditions have become steady, the observations are begun. Scrupulous care is taken to insulate the room and the surroundings of thermopile against external heat effects.

It must be acknowledged that the work was initiated by Mr. S. B. L. Mathur while he was in the Institute and we have to record our thanks to him for helpful suggestions in the early stages of the work. Our thanks are also due to Prof. Paranjpe for his constant encouragement and advice.

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THE PRESENT POSITION REGARDING THE THEORIES ABOUT THE NATURE OF ACTIVE NITROGEN

BY

C. R. DHODAPKAR.

In 1900 E. P. Lewis observed ^{2,7} that nitrogen could be stimulated by an electric discharge to emit a bright yellow glow which continued for some time even after the discharge had ceased. He photographed the infra-red portion of the spectrum and made a number of spectroscopic observations on the glowing nitrogen. Lord Rayleigh, who investigated the phenomenon in a more general and systematic way, discovered that the glowing gas had remarkable spectroscopic and chemical properties and named it 'Active Nitrogen'. Active Nitrogen could be produced in a number of ways. Kaplan¹⁰ produced it by passing condensed discharge through air at 0.5 m.m. Herzberg showed that it was possible to produce active nitrogen in which the percentage of nitrogen varied from 100 per cent. to 40 per cent. Hagenbach and Frey¹³ showed that glowing active nitrogen could be produced by passing condensed discharge through air at 10 m.m. The spectra observed by all these authors were the same as that obtained from active nitrogen that has been produced from almost pure nitrogen. It is, however, our experience that active nitrogen, as produced from almost pure nitrogen* is the most intense.

It may be mentioned, as a passing remark that a line spectrum due to the nitrogen atom is known, but is not shown by active nitrogen. Wien showed the emitting system of the *N₂ molecule the emitter.* nitrogen first positive bands to be uncharged. He allowed a stream of luminous gas to flow out of a canal tube into a space where a vacuum of the order 10^{-3} to 10^{-4} m.m. is continuously maintained by a number of diffusion pumps. In this space the gas is allowed to pass between two parallel plates which are maintained at a small distance apart at a constant difference of potential. The spectrum of the luminous slit-like region is photographed. Particles which are uncharged showed straight spectral lines, while lines due to charged particles are bent one way or the other. The vacuum in the space is so high that no collision takes place amongst the particles. Further Rayleigh was unable to con-

* The presence of a slight impurity is very essential for the production of active nitrogen.

dense anything which might indicate the existence of a body such as N_3 . It seems fairly certain therefore, that the characteristic luminescence is emitted by simple diatomic nitrogen molecules in some *unusual* State.

As has been said before, active nitrogen has remarkable spectroscopic and chemical properties. Its most conspicuous features are green, yellow and red bands*; the yellow ones, being usually the brightest, give the glow a yellow colour. The passage of a weak discharge through active nitrogen excites the fourth positive bands, but results, as was pointed out by Strutt, in the partial destruction of the afterglow. Heat has a peculiar effect on the afterglow. If a stream of glowing gas is passed through a tube which is moderately heated, the glow is locally extinguished, although it is still able to excite sodium atoms to the emission of the yellow doublet (¹¹, ¹², ¹⁸). If on the other hand, it is carried through a tube immersed in liquid air, it glows with increased luminosity. Active nitrogen reacts with metals, non-metals and compound bodies in a remarkable way. It excites the D and sometimes the green doublet of sodium, and also the line spectra of Cd, Mg, Hg, K, Zn, P, Th. It changes yellow phosphorus to red, forms a transparent green deposit with sulphur and reacts with several non-metals such as iodine, arsenic, etc. The reaction with nitric oxide is important; the gases interact with the production of a greenish flame, the evolution of heat and the formation of nitrogen peroxide and nitrogen. It develops the band spectra of compounds when they are vaporised in it, giving in many cases spectra of substances too unstable to be examined at the temperature of Bunsen flame. In fact this simplified development of the band structure constitutes a great advantage of active nitrogen over the arc or the spark in the study of band-spectra. It is true that the band system developed in this way often differs considerably in appearance from the same system developed in arc or spark on account of a radical change in the intensity distribution as regards both the intensity of the lines in each band and the relative intensities of the bands of the system. In its interaction with other substances, active nitrogen is able to transfer to atoms and molecules amounts of energy up to, but not exceeding, 9.4 though amounts up to 10.4 volts may be transferred under certain conditions.⁸

Various theories have been advanced to explain the nature of active nitrogen, and the mechanism of its formation and decay, but

* The system of bands referred to are the N_2 bands in the spectrum of active nitrogen belonging to the First positive System. $B^3 \pi \rightarrow A^3 \Sigma$. See Dr. Jevon's Report on Band-Spectra, P. 206.

as yet there is no theory which can explain all the characteristics, the properties, and the reactions of active nitrogen. The present is an attempt to throw some more light on this problem which still awaits a more satisfactory solution.

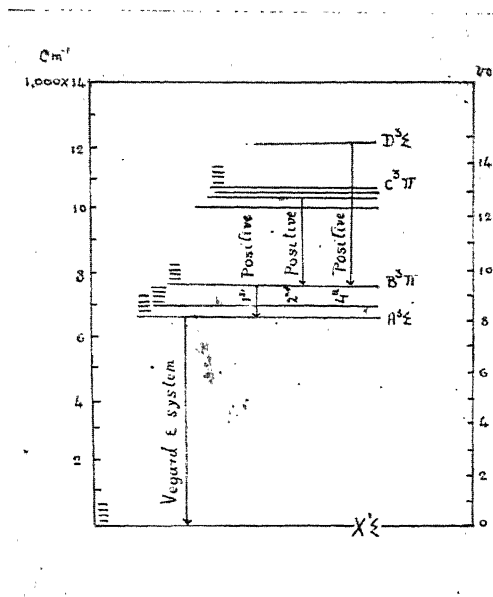
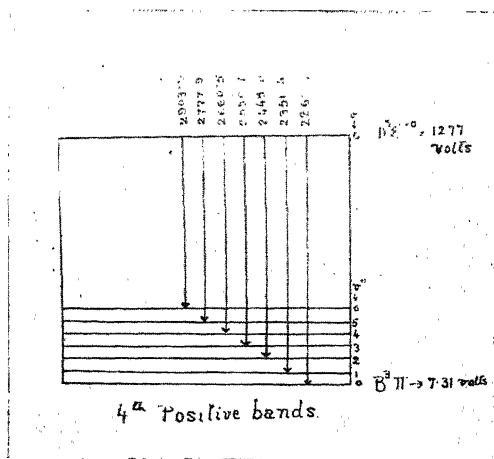
It has been said above that the presence of some impurity is essential for the production of active nitrogen. The emission of the spectrum of the afterglow is one in which nitrogen alone is concerned; the impurity simply plays the part of a catalytic agent, and is involved in no other way, for the spectrum is identical whether the impurity is oxygen, methane or any other gas.

We now come to the consideration of the mechanism by which active nitrogen is produced and suffers decay. We have obviously three possible views before us; (a) atomic nitrogen emerges from the discharge and then recombination takes place to give the molecules which are at an energy level high enough to give the known spectrum, (b) nitrogen atoms emerge from the discharge and in a triple collision that follows combine to form a normal molecule, the energy involved in the recombination process being utilised to excite a third partner, the normal molecule involved in the collision, to a higher energy level, (c) molecules of nitrogen excited in the discharge to a higher energy level are 'metastable'; that is, they have considerable life and can continue to exist for some time after leaving the discharge.

If we now assume (a) to be the possible mechanism, a spectroscopic difficulty arises, in that we should expect a certain amount of continuous spectrum as a result of the recombination of free atoms. There is yet another difficulty; unless the two atoms meet in a triple collision with a third molecule which can remove the energy liberated in the union of two atoms, there is every reason to expect that the energy so liberated in the recombination process would again break asunder the newly formed molecule into atoms. Thus if the mechanism involves the union of atoms into molecules, that recombination can take place only in triple collisions.

One of the main differences of the condensed and the uncondensed discharge in nitrogen is the excitation of the fourth positive group in the former, the null (0,0) band in this group requiring about 14.8 volts for its excitation. In order to obtain active nitrogen in any appreciable quantity, it is very necessary to use a condensed discharge. All the known fourth positive bands originate on the D level that has zero as its vibrational quantum number*. Bands arising on higher D levels have not been observed, suggesting that the binding in this state is so weak that dissociation

(*) Dr. Jevon's report on band-spectra, p. 77.



The figures on the right represent the values of excitation potential accepted until the discovery and interpretation of Vegard's $A \rightarrow X$ bands. They must be brought down by 2 to give the values at present accepted.

occurs quite readily. These facts suggested to Sponer the following hypothesis¹⁴ regarding the nature of active nitrogen. A discharge in which the molecules are on the brink of dissociation should according to Sponer abound in atoms. This and the long life of active nitrogen and its behaviour in the presence of catalysts suggest with reasonable certainty that active nitrogen is composed of normal atoms and molecules. The characteristic visible afterglow is emitted as a result of triple collision between two atoms and one molecule; the energy liberated during the recombination process of two atoms is in many cases sufficient to raise the third partner to the vibration level corresponding to quantum number twelve of the B state. Dr. Sponer's estimate of the dissociation energy¹⁴ was 11.5 volts, the energy which is necessary to excite these bands. But it is now difficult by her theory to account for the afterglow bands, as the work of dissociation of the nitrogen molecule has recently been estimated at about 7.34 volts* (the figure now accepted by all). Secondly her theory is unable to explain the exceptional enhancement of the bands corresponding to vibration quantum numbers 11 and 6 in the upper $B^3\pi$ state.

Before we go on to consider the mechanism (c), we will just consider the selection rules for electronic transitions for band-systems. They are

- (i) Change of $S=O$ usually or ± 1 less frequently; i. e. change of multiplicity $= O$ usually, or ± 2 less frequently.
- (ii) Change of $\lambda = O$ or ± 1 ; Change of $\Sigma = O$.
- (iii) Change of λ for 'emission' electron $= O$ or ± 1 .
- (iv) Of the three conceivable transitions between three given electronic states, all may take place in a compound molecule, but not more than two in an elementary molecule.

This extra restriction in the case of elementary molecules was interpreted by an application of the quantum mechanics. The elementary states of an elementary molecule are classed theoretically as "even" or "odd" according as the sum of the individual l -values for all electrons is even or odd, exactly as in the case of atomic states. Transitions occur only between states of opposite character, $g \rightarrow u$ and $u \rightarrow g$, and this rule, which is exactly the same for atoms, applies rigorously to elementary molecules. The molecule which emits the afterglow bands is N_2 , an elementary molecule. The N_2 states X, A, a, B and C are classed as $X^1\Sigma_g, A^3\Sigma_u, a^1\pi_u, B^3\pi_g$, and $C^3\pi_u$ respectively. The observed system $C \rightarrow B$ (2nd positive), $B \rightarrow A$

* Sponer and Herzberg determined the value of dissociation energy to be 734 volts (Zeits für Phys-Chem 26 B, 1, 1934) although the accuracy of their result is questioned by Appleyard, Thomson and Williams (Nature 134, 322, 1934). The figure 73 is now strongly supported by Maier-Leibnitz and Sponer (Z P 89, 431, 1934), Mulliken (P R, 46, 144, 1934) and Büttendörfer and Herzberg (Ann der Phys, 21, 577, 1935) and some of Kaplan's 1934 notes.

(first positive) and $A \rightarrow X$ Vegard's Σ system, are all according to this selection rule. But A is a triplet level, while X is a singlet level. The transition $A \rightarrow X$ is very feeble because of the inter-multiplicity. A is thus a metastable state to a certain extent.

Further from the Hund theory, we can predict the lowest three terms of atomic nitrogen to be 4S , 2D , and 2P , where 4S term is a normal one, and 2D and 2P are metastable states. The difference $^2D-^4S$ is found from Hopfield's data on the ionization limit of $N\ I$ to be 2.37 volts. The difference $^2P-^4S$ has been interpreted from the spectrum of $O\ II$ and is found to be 3.56 volts.

Cario and Kaplan¹⁸ considered that beside normal atoms and molecules, active nitrogen contains non-vibrating metastable molecules in the $A^3\Sigma$ state corresponding to an energy of 8.2 volts* in addition to two kinds of metastable atoms in 2D and 2P states corresponding to energies of 2.37 and 3.56 volts respectively. They explain the special enhancement of the bands corresponding to quantum numbers 11 and 6 in $B^3\pi$ state as a result of collision between metastable atoms and the metastable molecules, for the energies necessary to excite these bands are very nearly equal to 11.5 ($8.2+3.56$) and 10.5 ($8.2+2.37$) volts respectively. With this theory the 'dark modification' which can still excite D lines of sodium, the emission of the afterglow bands, as well as other properties could be satisfactorily explained.

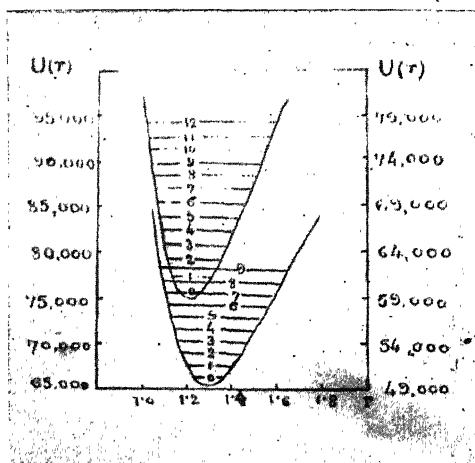
Assuming that in active nitrogen, metastable molecules and metastable atoms occur at proper concentration, the so-called resonance effect in the metallic spectra should be expected to occur, that is to say the lines corresponding to an excitation energy greater than that of the metastable molecules (8.2 volts) will be extremely weak in comparison with those which have their excitation energies equal to 8.2, 2.37, and 3.56, or smaller than 8.2. The more intense the lines appear, the nearer their excitation energies to 8.2, 2.37, 3.56, volts. No special enhancement of such lines was observed in the metallic spectra observed by several experimenters.

POTASSIUM †

| Line observed | Excitation energy | Remark. |
|---------------|-------------------|-------------------------|
| 1^2S-4^2P | 3.58 | No special enhancement. |
| 2^2P-4^2D | 3.38 | „ |
| 2^2P-3^2S | 3.38 | „ |

* State $A^3\Sigma$ was at that time supposed to have electronic energy of about 8.2 volts, but has recently been shown to have only 6.14. The state $B^3\pi$ has therefore 7.31 volts.

† The Science Reports of the Tohoku Univ. vol. 21, No. 4, p. 557, 1932.



Approximate potential energy curves for $A^3\Sigma$ and $B^3\pi$ States of N_2 . On the right are given the values now accepted of potential energy for $A^3\Sigma$ and $B^3\pi$ states of N_2 ; on the left are the values accepted until the discovery and interpretation of Vegard's $A \rightarrow X$ bands.

| Caesium† | | |
|---------------|-------------------|---------|
| Line observed | Excitation energy | Remark. |
| 1^2S-5^2P | 3 42 | " |
| 2^2S-6^2P | 3 55 | " |
| 2^2P-6^2D | 3.43 | " |
| 2^2P-7^2D | 3.56 | " |
| Mercury† | | |
| 2^3P-2^1S | 7.89 | " |

It is to be concluded from the above that as there is no evidence of resonance enhancements, the concentrations of such metastable atoms and molecules, if they exist at all in active nitrogen, is negligible. On the other hand, it is generally observed that in active nitrogen, lines of lower excitational energy appear, without any exception, to be more intense than those of higher excitational energy, and that the decreasing rate of the intensities of the lines with the increase of term number is more rapid in this case than in any other case of excitation (^{3,4,6}). Again the long life of active nitrogen which is its important feature cannot be explained by the existence of metastable atoms and molecules. Besides from the results of exhaustive experiments carried out by Herzberg¹⁶, Kneser,¹ Waredé¹⁷ Bay and Steiner²¹ it is at present generally accepted that active nitrogen is composed of nitrogen atoms and that its main properties are natural consequences of its atomic nature.

J. Okubo and H. Hamada⁹ accepted Spomer's hypothesis regarding the nature of active nitrogen, namely that active nitrogen is composed of normal atoms and molecules. They have made, however, two assumptions to explain the observed results and properties of active nitrogen. They assume in the first instance that in the vibrational states with $v'' = 8$ in the metastable $A^3\Sigma$ state and that corresponding to $v' = 6$ in the upper $B^3\pi$ state, the near-nuclear turning points have the same nuclear distance as the nuclear separation between the nuclei in the normal $X^1\Sigma$ molecular state. Secondly they assume that with the exception of neutral unexcited atoms and molecules, molecules corresponding to quantum numbers 7 or 8 of the metastable $A^3\Sigma$ state are the most numerous. With these assumptions, they suggest that the nitrogen molecules are excited to the required energy levels in two steps, the first being the excitation to the metastable $A^3\Sigma \sim^8$ state and the second to the $B^3\pi \sim^{11}$ and $B^3\pi \sim^6$. Most of the properties of active nitrogen can then be explained by this modified view.

It is however doubtful if the two assumptions made have really the experimental backing they need. The Morse function that they have used to find the near-nuclear distances gives the values very

† The Science Reports of the Tohoku Univ. vol. 21, No. 4, p. 557, 1932.

approximately. Secondly it will also be seen from the diagram that the potential energy curves for $B^3\pi$ and $A^3\Sigma$ states on the left hand side run almost steep and it will be equally accurate to say that the nuclear distances for some quantum numbers other than 8 for the $A^3\Sigma$ state and those for some quantum numbers other than 6 for $B^3\pi$ state are equal to the nuclear separation of the nuclei in normal $X^1\Sigma$ state. Further J. Okubo and H. Hamada take it for granted that the dissociation energy of the nitrogen molecule in the $X^1\Sigma$ state is greater than the excitation energy for the $A^3\Sigma \sim^8$ state. The exact determination of these energies is very necessary, since their values are nearly equal to each other. Their whole hypothesis falls to the ground, if it be shown that the energy of the $A^3\Sigma \sim^8$ is greater than the energy of dissociation.

G. Cario²⁰ who with Kaplan¹⁸ had assumed the existence of metastable molecules and metastable atoms to explain the emission bands of active nitrogen now considers that active nitrogen is atomic in nature and recombination of two normal nitrogen atoms to molecules is possible only in triple collision. Molecules so produced are in an excited metastable state. Collision between two such molecules gives rise to a metastable 2P atom and normal 4S atom, or two atoms in the 2D state and a normal molecule in each case. These metastable atoms collide with metastable molecules raising them to higher energy levels from which they emit the afterglow bands.

The arguments advanced for the production of metastable molecules and metastable atoms are worthy of careful attention. Cario accepts 7.34 volts as the value of the dissociation energy as determined by Sponer and Herzberg¹⁹, and 6.14 volts as the value of the ground level of the A state as against 9 and 8.3 volts respectively. So far as the mechanism of the emission of the afterglow is concerned the quantitative data do not matter, although it may be remarked that the accuracy of these data is questioned by some experimenters⁶ and supported by many others. To follow Cario then, two normal atoms and one normal molecule meet in a triple collision. In their recombination process, they liberate 7.34 volts of energy which raises the molecule to $A^3\Sigma \sim^7$, or to $A^3\Sigma \sim^0$. In the latter case the difference (7.34-6.14) will be used partly by the old and partly by the new molecule to change their translation energy. Metastable atoms are produced by collision of two metastable molecules. For a 2P atom the reaction would be

| | | | | | | |
|--------|---|--------|---|--------|---|----------------------|
| Volts. | | Volts. | | Volts. | | Volts. |
| 6.14 | + | 6.14 | = | 7.3 | + | 3.56 + a small part. |

The small amount of energy which remains unaccounted for would be used up by a 2P atom to change its translation or vibrational energies. For a 2D atom,

$$6.14 + 6.14 = 7.3 + 2.37 + 2.37.$$

In this case a very small amount would be left for changing the translation or vibrational energies.

It will be seen from the above reactions that in the collision between metastable molecules the number of ^2D atoms produced on an average should be twice as great as the number of ^2P atoms produced. Interpreted spectroscopically this means that in the spectrum of active nitrogen, bands from $\text{B}^3\pi\sim^6$, $\text{B}^3\pi\sim^5$ etc. should be more intense than those arising from $\text{B}^3\pi\sim^{11}$ etc. This is quite in contradiction to the observed distribution of intensity in the afterglow, where, bands arising from $\text{B}^3\pi\sim^{11}$ being the most intense, ^2P atoms must obviously be the more abundant of the two. This constitutes clearly a contradiction between experience on the one hand and theory on the other. Cario's present hypothesis is still open to the objection that no impact resonance in metallic vapours is experienced, in spite of the production of metastable atoms and molecules in the process.

It will be clear from the foregoing pages that although there is no doubt as to the atomic nature of active nitrogen, the special enhancement of the bands arising from $\text{B}^3\pi\sim^{11}$ state is still inexplicable. Of the two assumptions made by J. Okubo and H. Hamada, one at least has now the experimental backing after the determination of dissociation energy at 7.34 volts by Sponer and Herzberg which is greater than the excitation energy for $\text{A}^3\Sigma\sim^3$. As has been shown before, their other assumption is still very unconvincing, and as such the special enhancement of the bands arising from $\text{B}^3\pi\sim^{11}$ state cannot be explained, as they claim, on the Franck-Condon principle. We could, of course, see from Cario's theory that the bands arising from $\text{B}^3\pi\sim^{11}$ and $\text{B}^3\pi\sim^6$ should be more intense than those arising from other levels of $\text{B}^3\pi$ state. But looking to the portion in which the metastable atoms in the ^2P and ^2D states are produced according to Cario's theory, the bands arising from $\text{B}^3\pi\sim^6$ should be the most intense—a conclusion falsified by experiment. Cario's theory is still open to the objection, that in spite of the production of the metastable molecules and metastable atoms in triple collisions, no impact resonance in metallic vapours is experienced.

It has been said in the beginning that the presence of foreign matter is very essential for the production of active nitrogen. It therefore yet remains to consider the part thus played by the small proportion of foreign gases in its production. We have seen that the afterglow bands are due to the N_2 molecule alone. The impurities play no part in the actual light emission process. Their function must therefore be in

Part played by
foreign matter.

some way to accelerate the formation of atoms into excited molecules in the discharge, or to retard the spontaneous reversion of the active nitrogen which, in their absence, may be very rapid indeed. The work of Wood and Bonhoeffer in their investigation on hydrogen and the process of chemiluminescence provides us with a suitable analogy which, when applied to active nitrogen, probably explains the point in question. Wood and Bonhoeffer have shown that in a discharge tube filled with slightly impure hydrogen, the gas is completely dissociated in those parts of the tube which are far from electrodes, and can be pumped in a monoatomic form by a fast pump into a connecting tube. The walls of the tube cause a catalytic recombination of hydrogen atoms into molecules, and the impurities in the gas such as oxygen etc. act so as to hinder the catalytic recombination of atoms into molecules by the walls of the tube. The 'impurities' in nitrogen could have an exactly similar effect in preventing the destruction of atomic nitrogen in a 'useless' wall reaction.

SUMMARY.

1. A short account is given of the properties and phenomena of active nitrogen and also of the different methods of producing it. It is shown that the first positive system, $B^3\pi \rightarrow A^3\Sigma$ is due to N_2 molecule.

2. Three possible views of the mechanism by which active nitrogen is produced and suffers decay are discussed. It is now admitted that active nitrogen is atomic in nature, but none of the two theories discussed in the article explains convincingly the special enhancement of the bands arising from $B^3\pi \sim^{11}$ state.

3. An account is given of probable part played by foreign matter which is essential for the production of active nitrogen.

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A NOTE ON INTERPOLATION—FORMULAS.

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So many different formulæ for Interpolation are come across in a text-book that one is led to feel that each of them has some special feature and utility of its own. There is, for example, the Newton-Gregory's (or simply Newton's) formula for equal intervals of the argument and Newton's and Lagrange's ones for unequal intervals. Besides there are several central-difference formulas associated with the names Gauss, Stirling, Bessel, Everett, etc. As the fundamental principles on which these are based are the same, one would expect the same degree of accuracy from all and it is the object of this article to show that this is really the case. The special claims for accuracy that are advocated by a number of authors in favour of the central-difference formulæ over the Newton-Gregory formula can thus be seen to be ill-founded. On the other hand, the simplicity of form of the latter places it in advantageous position as compared with the former. I would therefore suggest that only two fundamental formulas, viz. those of Newton, one for equal and the other for unequal intervals of the argument, be laid emphasis on and used by *practical* statisticians and computers together with the working rule pointed out later in this article. (See Whittaker and Robinson's *Calculus of Observations* or the formulas and bibliography on the subject).

All interpolation formulas are derived from the following principles.

(i) The difference (or divided difference) of n -th order is constant (or practically so) and the subsequent differences are zero (or practically zero); the value of n depending on the function to be interpolated.

(ii) A polynomial of degree n is the simplest equivalent function.

(iii) The interpolation formula is this equivalent polynomial which exactly assumes the same values as the given function for the $(n+1)$ given values of the argument; and this is *supposed to be nearly equivalent* to the given function for all intermediate values of the argument.

Now, a polynomial of degree n , viz.

$$y = a_0 + a_1x + a_2x^2 + \dots + a_n x^n$$

has $(n+1)$ constants as coefficients and so, *one and only one* polynomial can be obtained which will have given values for $(n+1)$ given values of x . Or, putting it graphically, one and only one curve of n -th degree can be made to pass through $(n+1)$ given points of the function to be interpolated, that is, whose abscissæ represent the given values of the argument and ordinates the corresponding values of the function. It means that the graphs of the so-called different interpolation formulas must be identical. Hence the results of calculation from the various formulas must be identical too.

Next comes the important question of determining the region of the range (or interval) of the argument for which the equivalence of the polynomial with the function shall be the greatest possible. Before one can come to a satisfactory conclusion on this point, it is necessary to go over the process of deduction of an interpolation formula.

As the graph of the function to be interpolated is not known, only its values for some isolated values of the argument being known, the object of interpolation is to obtain an approximate form of the same which would be as accurate as possible. Since the given values of the function lead to the constancy (or practical constancy) of the n -th difference,—the value of n being obtained by actual calculation of the differences, one can see that in this respect the function behaves as a polynomial of n -th degree. Advantage is taken of this similarity in assuming that the polynomial will *very approximately* represent the function for the intermediate values of the argument. In other words, it is assumed that the graph of this polynomial would very approximately be the graph of the function in this range. There is no other valid ground for making this assumption except perhaps that of "simplicity", viz. that of the graph of the polynomial being the algebraically simplest curve which can be drawn through $(n+1)$ given points. In the case of absolute constancy the polynomial can be identified with the function in question.

Now, the degree to which the graph of the polynomial will approach the unknown graph of the function depends on the range or the interval within which the given values of the argument are distributed. It has been found from the actual study of a number of known graphs in relation to those of polynomials that

- (1) the smaller the interval the greater is the approximation; and
- (2) the closeness is most marked, in general, near the middle of the whole interval.

One can therefore safely assume that the same will be true for interpolation as well. That is,

(1) the smaller the given range of the argument the nearer is the approach of the polynomial to the function in question; and

(2) the nearest approach is, in general, near about the middle of the whole interval.

One must not forget the case when absolute constancy of the n -th difference is not forthcoming. In this case the degree of approximation of the interpolation formula will be less satisfactory than in the other one. This will be the lesser if the fluctuation in the values be greater. But here also the approximation will be the closest possible near about the middle of the whole interval.

The remark of the preceding paragraph also applies to the case when the formula is not proceeded upto that order of difference which is constant. One thus arrives at a simple *working rule* about all interpolation formulas, viz. *that the best results are obtained near the middle of the complete interval taken into consideration*. The central-difference formulas automatically take this into account; but the Newton's formula is bound to give the same result if the value to be interpolated be taken near the mid-range. An illustration is given below in support of this assertion.

The following example is selected from Whittaker and Robinson's *Calculus of Observations*, page 41, because it has already been demonstrated there that the answer as calculated with the help of all central-difference formulas is the same and equal to 0.0283 8498 7557, correct upto twelve decimal places. It only remains to show that the Newton's formula leads to the same answer.

Ex. To compute the value of $\log_{10} \cosh 0.3655$ from the following table:

| Argument | Function | Δ | Δ^2 | Δ^3 | Δ^4 | Δ^5 |
|----------|------------------|------------|------------|------------|------------|------------|
| 0.360 | 0.0275 5462 3980 | | | | | |
| 0.362 | 278 5523 7805 | 30061 3825 | | | | |
| 0.364 | 281 5737 9665 | 30214 1860 | 152 8035 | | | |
| 0.366 | 284 6104 7438 | 30366 7773 | 152 5913 | -2122 | -13 | |
| 0.368 | 287 6623 8989 | 30519 1551 | 152 3778 | -2135 | | 10 |
| 0.370 | 290 7295 2180 | 30671 1391 | 152 1640 | -2138 | -3 | |

As the differences upto the fourth order are, in the first instance (same as in the book), to be included in the calculation the corresponding polynomial must be of the fourth degree also, and must pass through five points. It is therefore necessary to omit one of the six given values and two results will be obtained according as the

first or the last five values are chosen. The corresponding Newton's formula is

$$f(a+xw) = f(a) + x\Delta f(a) + \frac{x(x-1)}{1\cdot 2}\Delta^2 f(a) + \frac{x(x-1)(x-2)}{1\cdot 2\cdot 3}$$

$$\Delta^3 f(a) + \frac{x(x-1)(x-2)(x-3)}{1\cdot 2\cdot 3\cdot 4}\Delta^4 f(a)$$

Taking the first five values, one gets

$a = 0.360$, w (or the equal interval) $= 0.002$, and so

$$xw = 0.3655 - 0.360 = 0.0055;$$

whence $x = \frac{55}{20} = \frac{11}{4}$. Therefore,

$$\begin{aligned} f(0.3655) &= 10^{-12} \times \left[(275\ 5462\ 3980) + \frac{11}{4} (30061\ 3825) \right. \\ &\quad \left. + \frac{77}{32} (152\ 8035) - \frac{77}{128} (2122) + \frac{77}{2048} (13) \right] \\ &= 10^{-12} \times [283\ 8498\ 7556.94] \dots\dots (1) \\ &= 0.0283\ 8498\ 7557, \end{aligned}$$

upto twelve decimal places. This is in agreement with the other results.

If, however, the last five values are chosen instead of the first five, one would have

$$a = 0.362, w = 0.002 \text{ and } x = \frac{35}{20} = \frac{7}{4}.$$

Therefore

$$\begin{aligned} f(0.3655) &= 10^{-12} \times \left[(278\ 5523\ 7805) + \frac{7}{4} (30214\ 1860) \right. \\ &\quad \left. + \frac{21}{32} (152\ 5913) + \frac{7}{128} (2135) - \frac{35}{2048} (3) \right] \\ &= 10^{-12} \times [283\ 8498\ 7557.12] \dots\dots (2) \\ &= 0.0283\ 8498\ 7557 \end{aligned}$$

as before.

If one desires to take all the six values of the Table into account the term involving the fifth order difference in the Newton's formula is to be added as well. This will add .09 to the number in the square brackets in (1) giving the result as

$$10^{-12} \times [283\ 8498\ 7557.03] \dots\dots (3)$$

It is of great interest to compare the results of calculation as given in the book (loc. cit.) upto fourteen decimal-places. These are

- (i) Everett's formula 0.0283 8498 7557 03,
- (ii) Bessel's formula 0.0283 8498 7557 02,
- (iii) Gauss's formula 0.0283 8498 7556 95,
- (iv) Stirling's formula 0.0283 8498 7556 94.

The difference in the last two figures of the above four results and that of (1) is due to the fact that in Gauss's and Stirling's formulæ (from which the calculations are made) as well as in (1), the term involving the fifth order difference is not taken into account; whilst that term is partially included in Bessel's formula and wholly in Everett's during the process of deduction of these formulas. The necessary corrections are 09 for each of the first three mentioned above and 01 for Bessel's; these bring the results equal to (3) in every case except Gauss's. The reason for the defection in the case of Gauss's formula might be adduced to some error in calculating the proper figure for the last place. Such concurrence in the results given by the various formulas is really to be expected since all central difference formulæ are deduced from Newton's formula for unequal intervals. And since the Newton's formula for equal intervals is merely a particular case of that for unequal intervals, and a central difference formula is for equal intervals too, one can expect a direct deduction of the latter from the Newton's formula for equal intervals. One method is based on Fraser's Lozenge Diagram. As an illustration of another but similar method, let us deduce Everett's formula viz.

$$\begin{aligned}
 f(a+xw) = & \left[\zeta + \frac{\zeta(\zeta^2-1)}{3!} \delta^2 \right. \\
 & + \frac{\zeta(\zeta^2-1)(\zeta^2-4)}{5!} \delta^4 + \dots \left. \right] f(a) \\
 & + \left[x + \frac{x(x^2-1)}{3!} \delta^2 \right. \\
 & + \frac{x(x^2-1)(x^2-4)}{5!} \delta^4 + \dots \left. \right] f(a+w) \dots (4)
 \end{aligned}$$

where $\zeta=1-x$ and $\delta^2 f(a) = \Delta^2 f(a-w)$, $\delta^4 f(a) = \Delta^4 f(a-2w)$ etc., from the Newton's formula

$$f(b+xw) = f(b) + x \Delta f(b) + \frac{x(x-1)}{2!} \Delta^2 f(b) + \dots \dots \dots (5)$$

Let us assume that the difference of order $2r$ is constant and form the following table:

| Argument for Newton's formula | Argument for Everett's formula | Function | Differences |
|----------------------------------|-----------------------------------|-------------------------|-------------|
| b | $\frac{a-rw}{a-r-1w}$ | $f(b)$ or $f(a-rw)$ | ... |
| $b+w$ | $a-r-1w$ | $f(b+w)$ or $f(a-r-1w)$ | ... |
| ... | ... | ... | ... |
| ... | ... | ... | ... |
| $b+r-1w$ | $a-w$ | $f(b+r-1w)$ or $f(a-w)$ | ... |
| $b+rw$ | a | $f(b+rw)$ or $f(a)$ | ... |
| $b+r+1w$ | $a+w$ | $f(b+r+1w)$ or $f(a+w)$ | ... |
| ... | ... | ... | ... |
| ... | ... | ... | ... |
| $b+2rw$ | $a+rw$ | $f(b+2rw)$ or $f(a+rw)$ | ... |

Here we have $a = b + rw$. Substitute this in the right-hand side of (4) and expand the various terms in terms of $f(b)$ and differences of $f(b)$ with the help of the Newton's identity and the associated ones, (since x happens here to be integral)

$$\Delta f(b+xw) = \Delta f(b) + x \Delta^2 f(b) + \frac{x(x-1)}{2!} \Delta^3 f(b) + \dots \quad (6)$$

$$\Delta^2 f(b+xw) = \Delta^2 f(b) + x \Delta^3 f(b) + \frac{x(x-1)}{2!} \Delta^4 f(b) + \dots \quad (7)$$

etc. Collecting terms we get

the coefficient of $f(b) = (1-x) + x = 1$;

the coefficient of $\Delta f(b) = r(1-x) + (r+1)x = (x+r)$;

the coefficient of $\Delta^2 f(b) = \frac{(x+r)(x+r-1)}{2!}$ on simplification;

and so on. Hence the right-hand side of (4)

$$= f(b) + (x+r) \Delta f(b) + \frac{(x+r)(x+r-1)}{2!} \Delta^2 f(b) + \dots$$

$$= f(b+xw+rw), \quad \text{by Newton's formula}$$

$$= f(a+xw)$$

since $a = b + rw$.

In conclusion I assert once more that Newton's formulas, one for equal and the other for unequal intervals of the argument, are the best ones to be used for interpolation, and that they should be used to interpolate near about the middle term. The central-difference formula of Gauss or Stirling or Bessel would also give the same result provided one writes down *all possible terms* as would be known from the difference Table. Everett's formula would give as good a result if only the number of values of the argument given in the Table is *even* as had been the case in the example considered in this paper; otherwise the result deduced will be inferior to those of the other formulas,

A CRITICAL SURVEY OF THE VALENCY-DEFLEXION HYPOTHESIS

By

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The Valency-deflexion Hypothesis which is associated with the names of Professor J. F. Thorpe and Professor C. K. Ingold was put forward to explain the numerous discrepancies in the relative case of formation and stability of the various ring systems on the basis of Baeyer's Strain Theory. A glaring instance of the failure of the Strain Theory of Baeyer is afforded by the experiments of Stohmann and Kleber (J. Pr. Chem. 1892 (11), 45, 475) on the heats of formation of simple homocyclic rings. The values of heat of absorption found by these investigators are at variance with the deduction of the Strain Theory.

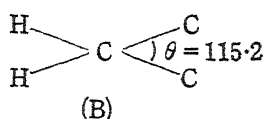
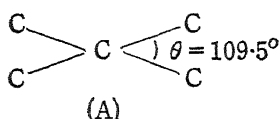
| Ring. | Cyclopropane. | Cyclobutane. | Cyclopentane. | Cyclohexane. |
|-----------------------------------|---------------|--------------|---------------|--------------|
| Angle of Strain Baeyer | 24.7° | 9.7° | 0.7° | 5.3° |
| Heat absorbed in cal., (S & K) | 38.1 | 42.6 | 16.1 | 14.3 |

If we plot the curves of instability, the thermal data indicates that Cyclobutane should occupy the crest of the curve, while, according to Baeyer, the Cyclopropane ring should possess the greatest instability. Secondly the Cyclohexane ring is the most stable, according to the thermal figures, while this place should be occupied by the Cyclopentane ring. Moreover, the difference between the thermal data for Cyclohexane and Cyclopentane is very small, while Baeyer's Strain Theory leads us to expect an appreciable difference in stability between them.

In spite of a large amount of experimental work stimulated by this theory, general experience supports the validity of the results of Stohmann and Kleber rather than the Strain Theory. Thus it has been found that the methods which give Cyclopropane, Cyclopentane

and Cyclohexane rings with the greatest ease, break down absolutely in the case of Cyclobutane ring. Moreover, there is an overwhelming amount of data in literature to show that the stability of the Cyclopentane and Cyclohexane rings is of the same order.

In order to explain this discordance, Ingold (J. C. S 1921, 305) assumed that the tetrahedral angle of Baeyer (109.5°) was only valid when the tetrahedron representing the Carbon atom was attached to four Carbon atoms (A). However, in the case of polymethylene rings, we are dealing with a secondary carbon atom (B). Now, as the investigations of Kopp, Traube and others have shown that the hydrogen atom in organic compounds occupies a smaller volume than the carbon atom, the two carbon atoms attached to the central one occupy more of the surrounding space than the two hydrogen atoms in the methylene group. In that case, the angle between the carbon atoms of the methylene group will not be 109.5° , as supposed by Baeyer, but something greater than this. Further, allocating a spherical domain, the cubic content of which is proportional to the atomic volume of the element, to each of the four atoms of the polymethylene group, and using the Traube values of atomic volumes of the carbon and hydrogen atoms (Ahren's Vortrage, 1899, 4, 255), and making other assumptions, Ingold calculated that this angle θ must be 115.3° , and not 109.5° , as hitherto assumed.

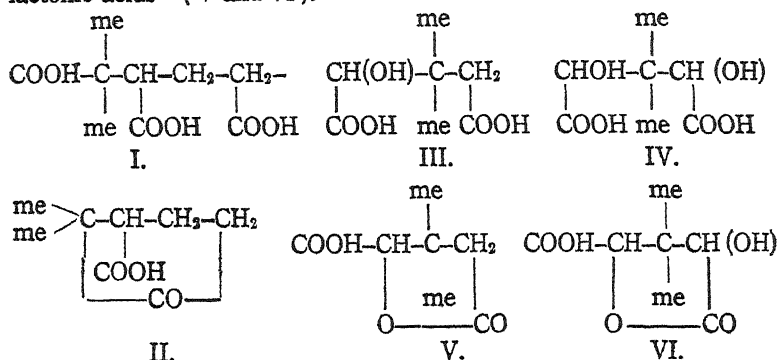


On the basis of this new value, it is possible to calculate by how much the terminal Carbon atoms of normal propane and butane chains must approach one another to form cyclopropane, and cyclobutane rings. The "*Approach values*" thus obtained are as follows and are in keeping with the thermal data of Stohmann and Kleber.

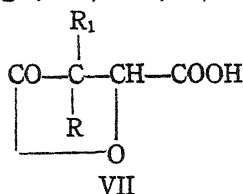
| Cyclopropane. | Cyclobutane. | Cyclopentane. | Cyclohexane. | Cycloheptane. |
|---------------|--------------|---------------|--------------|---------------|
| 0.345 | 0.427 | 0.220 | 0.207 | 0.730 |

The effect of gem-grouping in promoting ring formation is known in literature from the synthetical work of a large number of investigators. Thus Perkin and Thorpe (J. C. S. 1904, 85, 138) found that α - α -dimethylbutane α - β - δ -tricarboxylic acid (I) gave smoothly the cyclopentanone derivative (II) merely on boiling its sodium salt with acetic anhydride, while simple adipic acid did not undergo this change. α -hydroxy and α - α^1 -dihydroxy glutaric acids are stable substances, whereas the corresponding derivatives of β - β dimethylglutaric acid (III and IV) cannot be

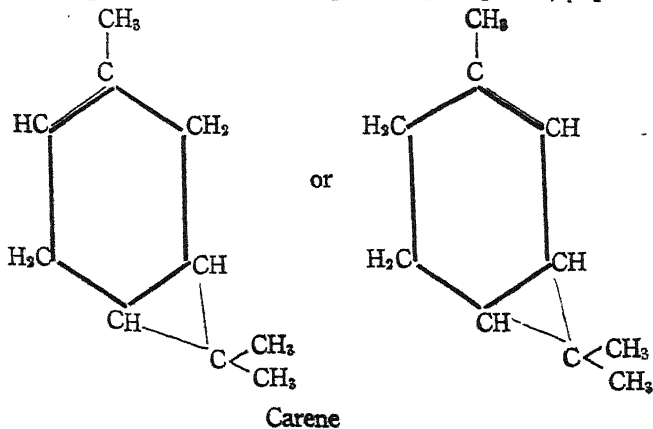
isolated in free condition owing to their tendency to pass into lactic acids—(V and VI).

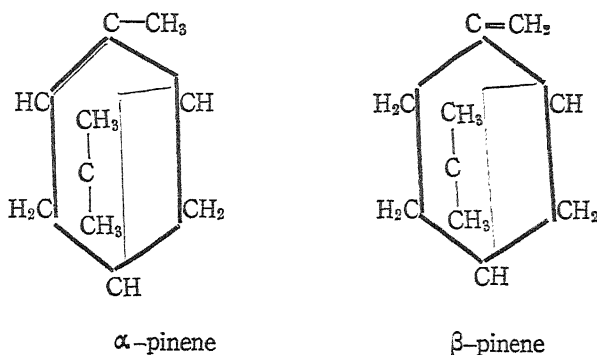


Glutaric anhydride is easily decomposed by water; β - β -dimethylglutaric anhydride may be boiled with water without much apparent change, whilst β - β - α -trimethylglutaric anhydride can be crystallised from hot water. (Perkin and Thorpe, J.C.S. 1899, 75, 65). A good number of β -lactones (VII) containing the gem-dialkyl groupings have been recently isolated (Kandiah, J.C.S. 1932, 1215; also Bæyer and Villiger, Ber, 1897, 30, 1955).



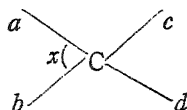
Among the naturally occurring essential oils, a large number of products contain the highly strained cyclopropane and cyclobutane rings, but the inherent strain of these compounds is relieved by the presence of a gem-dimethyl group e.g. carene, α -pinene, β -pinene.





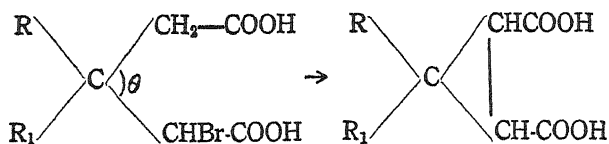
Camphor and Camphene also contain a gem-grouping, but simple monocyclic terpenes like limonene, α terpeneol, sylvestrene, pulegene, carvone etc. do not contain this grouping.

All these facts can be plausibly explained by the valency Deflexion Hypothesis which assumes that when a normal angle between the two valencies a and b of a carbon atom is changed either through their attachment to heavy groups or their inclusion in a ring complex, the angle between the valencies c and d undergoes a corresponding change in the opposite direction. Thus if the angle x becomes greater than normal angle 109.5° , the angle θ will be smaller than this amount, with the result that the groups attached to the valencies c and d will converge to one another.



The experimental support to this hypothesis has been given by so much amount of work that it is impossible to refer in details to all the work published by Thorpe, Ingold and their collaborators. (Beesely, Ingold and Thorpe, J.C.S. 1915, 107, 1080; Ingold and Thorpe, Ibid, 1928, 1320; Ingold, ibid, 1921, 305, 951 etc; Gane and Ingold, Ibid, 1928, 1954, 2267; 1929, 691; 1931, 2553. Qudarati Khuda, Ibid, 1929, 1913; 1930, 206 etc. S.S.G. Sircar, Ibid, 1927, 600, 1252, 1257; 1928, 898. K. A. N. Rao, Ibid, 1929, 1954; 1930, 1164. A. Kandiah, Ibid, 1931, 952). However, it is necessary to refer briefly to the three lines of evidence brought forward. (1) The work on the formation and stability of spiro-compounds formed by the removal of HBr from the two acetic acid residues of β - β -disubstituted glutaric acids as follows.

AA



The results tabulated below show that as the value of θ decreases, the stability of the spiro-acids increases.

| R R ₁ | Angle θ | Stability of the spiro-acids |
|------------------|------------------------------|--------------------------------------|
| Me, Me | 109.5° | Rapidly decomposed by 5% HCl at 200° |
| Cyclopentane | 109.7° | Rapidly decomposed by 5% HCl at 200° |
| Cycloheptane | 107.2° | Unaltered by cone-HCl at 240° |
| Cycloheptane | 109.5°-y where y is small | Decomposed by 20% HCl at 240° |
| Trans-decalin | 109.5°-x where x is small | Decomposed by 10% HCl at 240° |

(Cf the Annual Reports of the Chemical Society, 1930 page 155).

But the most important evidence brought forward by Thorpe and his co-workers was the study of the tautomerism of various α keto- β - β -disubstituted glutaric acids to the isomeric hydroxy-ring acids in presence of 64% potash. It was definitely shown that the percentage of the ring hydroxy acid in the equilibrium mixture increased as the angle θ decreased.

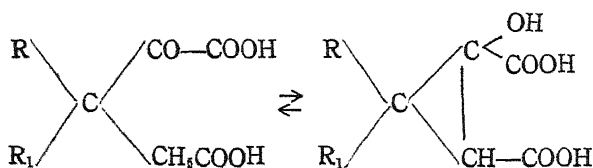


Table II shows the relation between angle θ , and the percentage of the ring hydroxy acid in the equilibrium mixture.

Table II

| R R ₁ | Angle θ | Percentage of the ring hydroxy acid | K ₁ at 25° × 10 ⁵ |
|------------------|----------------|-------------------------------------|---|
| H, H, | 115.3 | 0 | 4.69 |
| Me, H | 109.5 | 0 | 6.00 |
| Et, H | ? | 0 | 5.29 |
| Cyclopentane | 103.7 | 0 | 17.3 |
| Me, Me | 109.5 | 0 | 19.8 |
| Me, Et | 109.5-x | 0 | 24.4 |
| Et, Et | 109.5-y | 62 | 33.9 |
| Pr, Pr | 109.5-z | 71 | 33.9 |
| Cyclohexane | 107.2 | 100 | 33.4 |

The physical evidence of the dissociation constants of the various β - β -disubstituted glutaric acids (Spiers and Thorpe J. C. S. 1925 127, 538) is based upon the assumption that the greater the proximity of the two carboxyl groups to one another, the greater is the enhancement of the primary dissociation constant (K_1). The value of these dissociation constants have been shown above in table II.

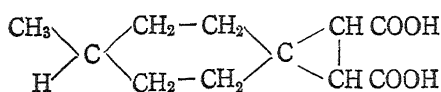
So far, we have discussed only one side of the *valency deflexion* hypothesis. Even during the early days of this hypothesis, a suggestion was raised that the effects of the associated groups and rings could be explained by some cause other than that of the valency-deflexion, such as the repulsion of electrically similar alkyl groups. But this objection can be waived aside when one takes into consideration the facile ring-closure of methyl diacetylsuccinic ester, where one of the methyls of the *gem*-dimethyl grouping is replaced by the carboethoxy group, whereas the unmethylated analogue does not undergo this change (Willstatter and Clarke, Ber, 1914, 47, 298,). Moreover, Lanfear and Thorpe (J. C. S. 1923, 123, 1683) found that the effect of the cyclopentane ring on the carbon tetrahedral angle was similar to that of *gem*-dimethyl group. On the other hand, if

valency-deflexion did not take any part, the effect of the cyclopentane ring should resemble that of the *gem*-diethyl group. The results obtained by Desai (J. C. S. 1932, 1065) in the decomposition of the mono- and dibromo-esters of 3-methylcyclopentane—1:1—diacetic acid showed that the methylcyclopentane ring bore the closest similarity to the cyclopentane and *gem*-dimethyl group, and not to the *gem*-ethyl-propyl group, which should be the case if valency deflexion was ruled out.

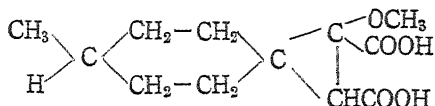
W. Hückel has severely criticised this hypothesis in a long memoir (Fortschritte der chemie, Physik und Physikalischen chemie, 1927, 19, 4.) disputing many of the fundamental assumptions of this hypothesis, but the authors have defended their original position (Ingold & Thorpe, J. C. S. 1928, 1318). Moreover, Huckel's memoir does not advance any constructive criticism in the form of an alternative hypothesis, which can satisfactorily collate all the data before the valency-deflexion hypothesis is given a knock out. Bennett and Chapman (Annual Reports of the chemical Society 1930, 155) are inclined to favour the opinion that a number of facts explained by the valency deflexion hypothesis can be ascribed to steric hindrance, especially the hydrolysis of the esters, the opening up of the lactones and the imides in which the screening effect of the substituents may be the principal factor. Short (Chem. News 1926, 133, 149) has pointed out that the "*Approach values*" calculated from the Bæyer value of θ (109.5°) agree with the thermal values of Stohmann and Kleber (Loc. cit) as well, as those calculated from Ingold's values of θ (115.3°). The absence of any single relation between the angles of strain, and the "*Approach values*" calculated from the Ingold value for θ has been pointed out by Gunjekar and Wheeler (J. Ind. Chem. Soci. 1932, 9, 87).

Finally, it is instructive, in this connection, to refer to the work of the author on the effect of the methylcyclohexane ring on the carbon tetrahedral angle on the basis of the valency deflexion hypothesis. It was observed that unlike the cyclohexane ring, it simulated the behaviour of the strainless rings like cyclopentane and trans-decalin. (Desai, J. C. S. 1932, 1047). That the mere introduction of a methyl group should have such a profound effect in eliminating strain is really curious and puzzling, and two explanations alone are possible. The methylcyclohexane ring may have become stabilised in the strainless form; but during the course of the investigation, all the efforts to isolate the isomeric spiroacids (VIII and IX) did not meet with any success. There used to be in literature, one instance of the isolation of four strainless isomeric forms of 4-methylcyclohexane—1-carboxy—1-acetic acid (X) by Qudarti Khuda (J. Ind.

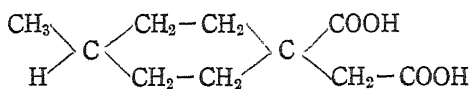
Chem. Soci 1931, 8, 277), but repetition of this work by the author and Dr. R. F. Hunter here in this Laboratory (in the press) has shown the existence of only two forms, and we have been independently supported in our conclusion by Goldschmidt and Grüfinger (Ber. 1935, 279).



VIII.



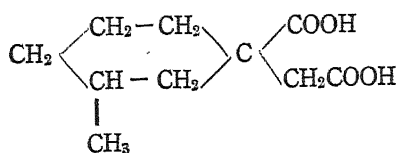
IX.



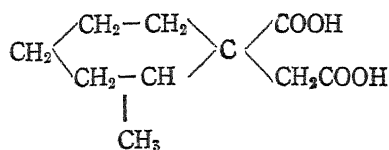
X.

Moreover, our attempts to obtain the four isomeric strainless forms of 3-methylcyclohexane —1-carboxy—1-acetic acid (XI) and 2-methylcyclohexane —1-carboxy—1-acetic acid (XII) resulted in the isolation of only two forms (in the press). We hoped for better luck in the isolation of two strainless forms of 3:3-dimethylcyclohexane—1-carboxy —1-acetic acid (XIII) where the *gem*-dimethyl group would stabilise the strainless forms, but we could get only one.

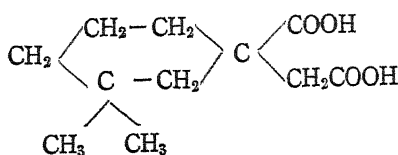
Finally, our exhaustive work (in the press) on the isomeric forms of 1-cyano-1-arylamino-4-methylcyclohexane, (XIV) and their 3-methyl- and 2-methyl-analogues convinces us that the methylcyclohexane and cyclohexane rings are similar in spatial configuration.



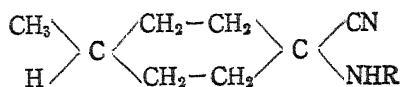
XI



XII



XIII.



(R = aryl.)

XIV.

To support this conclusion, there is another physical evidence in the form of the comparison of the primary dissociation constants of 3- and 4-methylcyclohexane, cyclopentane, and cyclohexane-1:1-diacetic acids. (Ives, Linstead and Riley, J. C. S. 1932, 1093) which are shown here under.

| Acid | K_1 at $25^\circ \times 10^4$ |
|---------------------------------------|---------------------------------|
| Cyclopentane-1:1-diacetic acid | 1.76 |
| Cyclohexane-1:1-diacetic acid | 3.23 |
| 3-methylcyclohexane-1:1-diacetic acid | 3.25 |
| 4-methylcyclohexane-1:1-diacetic acid | 3.21 |

The conclusion is unavoidable that the chemical methods used to demonstrate strain in cyclohexane, cyclopentane and other rings are invalid in the case of the methylcyclohexane ring. The author believes that it is not presumption on his part to say that these methods have been found wanting, in spite of their successful application in the previous cases, and that an ideal chemical method has yet to be discovered.

Summaries and Abstracts of Theses for the M. Sc. degrees.

1.—“*Dielectric Properties of Some Vegetable Oils.*” By Mr. P. Y. DESHPANDE. for the M. Sc. degree of the Bombay University. (Royal Institute of Science.)

The density, the refractive index and the dielectric constants at room temperature (26°C) are determined for the solutions of castor oil, olive oil, sesame oil, and coconut oil in benzene. The dielectric constants are determined at 30 meters (10,000 k. c.) by observing resonance with the help of a valve-voltmeter. The method of solution is used to establish the dipole character of the oil molecules and to determine the values for their polarizations and electric moments by the application of the Debye equation for dilute solutions of polar substances in non-polar solvents.

It is found that in very dilute solutions, the molecules of these oils are more or less free from association though at higher concentrations the association effects are predominant. Experiments on very dilute solutions of these oils therefore give fairly reasonable values for their electric moments which are in this case 3.678×10^{-18} , 3.030×10^{-18} ,

2.914×10^{-18} , and 2.821×10^{-18} for respectively castor oil, olive oil, sesame oil and coconut oil.

2—*Transmission of light through homogeneous clouds.* By Mr. N. N. BHAGWAT for the M. Sc. degree of the Bombay University (Royal Institute of Science, Bombay)

The work was undertaken to verify Stratton and Houghton's theory of the transmission of light through clouds of water.

The paper gives a method of analysis for the verification of the above theory and describes suitable experimental arrangements for obtaining the necessary data.

The results obtained with water are discussed in detail and are found to agree tolerably well with the theory, with all its limitations.

In order to obtain information about the influence of refractive index on transmission, six other typical liquids were also examined. Transmission curves for different wave lengths were found closer together in the case of lighter liquids but no definite conclusions could be arrived at as

regards the effect of the refractive index.

Two of these liquids showed good agreement with the theory; one liquid showed only a partial agreement; and the remaining three exhibited no agreement whatever.

3.—*Artificial vibrations of the ground.* By MUKUND DINKAR MANOHAR for the M. Sc. degree of the Bombay University. (Colaba Observatory, Bombay.)

When a known weight is dropped from a known height we communicate a definite energy into the ground. We can calculate the vibrations produced in the ground, assumed to be isotropic, by an impulse of this kind and compare them with the observed results. The ground movements at various distances from the source of disturbance were recorded by two horizontal components 'N. S. and E. W.' seismographs of the Milne Shaw type. (period twelve seconds, damping ratio 20 : 1 and a vertical component seismograph (period 3.6 seconds,) all locally constructed. All the three components were recorded on the same sheet of photographic paper kept quickly moving by clock-work. The movement in all the three components begins with a sudden impulse and is followed by oscillations having compound periods composed of the free periods of the small building in

which the instruments are housed and the forced periods of the ground due to the dropping of the weight. The amplitude of the horizontal component of the ground movement is found to decrease with distance approximately according to the theoretical law (distance)^{-1/2}. The periods of the forced movement of the ground depend on the duration of impact and the elastic constants of the ground; and the theoretical values agree fairly closely with the observed values. When a weight of 12.7 kilogrammes meets the ground with a velocity of 4 M/s, the amplitude of the horizontal component of the ground movement at Colaba is about 12 μ at a distance of 10 metres and 5 μ at 20 metres and the period of the forced vibrations is about 0.05 sec. The free period of the building is 0.014 sec.

4—*Evaporation and its measurements.* By NARAYAN VASUDEO KOGKAR for the M. Sc. degree of the Bombay University. (Bombay and Poona Observatories).

Guide: Dr. S. K. Banerji.

In continuation of the work on the subject by S. K. Banerji and H. M. Wadia (Memoirs of the India Meteorological Dept. Vol. XXV Part IX 1932) further experiments were carried on at Poona mainly with the object of studying the behaviour of the layer

next to the evaporating surface. For this purpose an evaporation tank ($2' \times 2' \times 1\frac{1}{2}'$) with the usual water channel all round was placed in a closed chamber with an arrangement for varying the radiation by an electric heater with parabolic reflector. A large number of open scale thermometers (dry and wet bulb) were arranged with axial symmetry and with their bulbs at various heights above the water surface. Thermometers were also installed for recording water temperature; a black bulb in vacuo was used for taking measurements of the radiation. An eye-reading evaporimeter was also observed at the same time. Starting with a known sample of air observations were taken with (1) water temperature varying, air temperature remaining constant, (2) water temperature constant but air temperature varying, (3) both water and air temperature varying. The observations indicate the existence of a layer of depth varying from 3 to 6 cms. according to the intensity of radiation and temperature of water, next to the evaporating surface with properties different from those of the layers above. These properties have been plotted and analysed in the paper. Records have been taken of the air movements above the evaporating surface by means of smoke lines. Some continuous records of evaporation in the open were also taken. These have been discussed in the paper.

AB

5.— *β -hydroxy-ethyl ethers of substituted phenols and related substances.* By D. C. MOTWANI and T. S. WHEELER. A summary of the thesis submitted by Mr. Motwani for the M. Sc. degree of the Bombay University. June 1934, (Royal Institute of Science.)

PART I. *β -hydroxy-ethers of substituted phenols.*

Part I deals with the condensation of ethylene chlorhydrin with resorcinol, *m*-methoxy phenol, resacetophenone, and 4-ethyl resorcinol, and derivatives of the products. The resultant hydroxy ethyl ethers of the type R. O. CH₂. CH₂OH, where R = substituted or unsubstituted benzene nucleus, may be antiseptics.

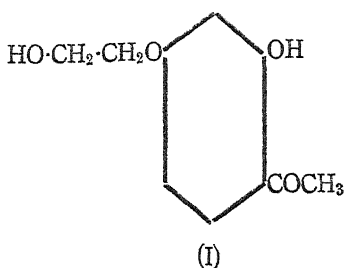
Rindfusz, Ginnings, and Harnake (J. A. C. S. 1920, 42, 157) condensed ethylene chlorhydrin with resorcinol in presence of sodium ethylate and obtained 1:3 di (β -hydroxy-ethoxy) benzene. The condensations have now been effected by dissolving the phenol in aqueous potash and refluxing the solution with ethylene chlorhydrin. The modification is noteworthy in that, in the case of insoluble ethers, the completion of the reaction is marked by the aqueous layer losing its colour which is initially red. It was observed that the heat of solution in the case of resacetophenone and 4-ethyl resorcinol affected the yield and isolation of the end-product. For this reason

these phenols were dissolved in alkali in presence of ice.

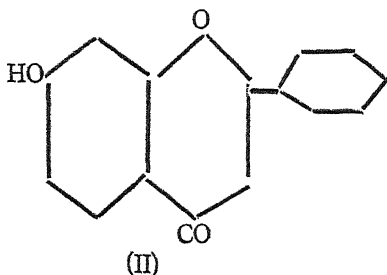
Resorcinol gave (a) *m*-(β -hydroxyethoxy phenol and (b) 1:3 di (β -hydroxy-ethoxy) benzene of which the former is new. The di-ether was obtained in purer state m. p. 95-96° Rindfus (loc. cit.) gave 81°.

m-methoxy phenol gave *m*-methoxy (β -hydroxy-ethoxy) benzene which is a liquid.

Resacetophenone gave only 2-hydroxy-4 (β -hydroxy-ethoxy) acetophenone (I).



Its constitution was fixed by the alcoholic ferric chloride coloration and the synthesis of 7-hydroxy flavone (II)



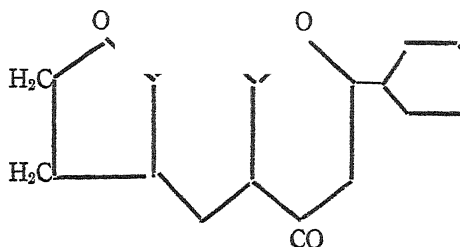
m.p. 240° (Robinson and Venkataraman J. 1926, 2, 2344). The alkali soluble benzoyl derivative of the ether separated as a gel from the usual organic solvents.

Alkali insoluble phenols were obtained from the ketone-ether. They were, the *azine*, the *anil*, the *phenylhydrazone*, and the *benzidine* condensation product HO. C₂H₄OC₆H₃ (OH). C (CH₃). NC₆H₄.C₆H₄NH₂. All these were insoluble in dilute aqueous alkalis (Cf. Adams, J.A.C.S. 1919, 41, 247). The reasons for this insolubility are still obscure and the phenomena are rendered still more difficult to explain by the observation now made that certain phenols though insoluble in dilute alkalis, dissolve when they are suspended in strong alkali and the system diluted with water. The ketone ether on reduction with zinc-amalgam gave 2-hydroxy-4 (β -hydroxy-ethoxy) ethyl benzene.

4-ethyl resorcinol gave (a) 2-hydroxy-4 (β -hydroxy-ethoxy, ethyl benzene) in a predominating yield and (b) 2:4 di (β -hydroxy-ethoxy) ethyl benzene. (a) was identified with the reduction product of I.

Part II. Condensation of 2-hydroxy-4 (β -hydroxy-ethoxy) acetophenone with aromatic aldehydes; an attempt to synthesise dihydrofuran flavone.

Part II describes an attempt to synthesise substances containing fused coumarane and γ -pyrone nuclei: dihydrofuranflavones (III).



(III)

The methods employed consisted in starting with either a coumarane or a flavone and introducing either the flavone or coumarane ring. The attempts in this direction did not lead to a successful synthesis of a dihydrofuran flavone, as coumarane derivatives could not be obtained. Some flavone derivatives have been prepared and studied. The starting materials chosen were the mono- β -hydroxy-ethyl ethers of resacetophenone and *m*-methoxy phenol.

(I) was condensed with benzaldehyde and the 2-hydroxy-4 (β hydroxy-ethoxy) chalkone converted by Kostanecki's method (Ber. 1898, 36, 1757) via diacetoxy-chalkone-dibromide into 7- (β hydroxy-ethoxy) flavone which on de-ethylation passed into (II). Direct bromination of 2-hydroxy-4- (β hydroxy-ethoxy) Chalkone introduced a bromine atom into the nucleus and the bromo derivative when hydrolysed yielded 7- (β hydroxy-ethoxy)-6-bromofla-

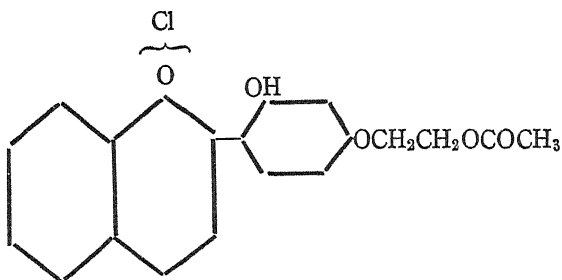
vone and not the isomeric benzylidene-coumaranone (cf. Cullinane and Phillpot J. 1929, II, 1761). The constitution of the

compound was arrived at by its colourless solution in concentrated sulphuric acid (Cf. Perkin & Everest; "The Natural Organic colouring matters" p. 164.) The compound on treatment with phosphorus pentabromide gave 7- (β -bromo-ethoxy)-6 bromoflavone.

(I) was condensed with O. nitrobenzaldehyde when corresponding chalkone was obtained and not a lactyl ketone (Cf. Claisen Ber, 1881, 14, 2470; Baeyer & Drewsen Ber, 1882, 15, 2856, and Price & Bogert J. A. C. S. 1934, 56, 2443). It was found that the sunlight affects the yield and the isolation of the chalkone and hence the condensation was carried out in absence of white light.

(I) was also condensed with anisaldehyde and salicylaldehyde when the corresponding chalkones were obtained. 2-hydroxy-4 (β hydroxy-ethoxy)-4-methoxy-chalkone derived from anisaldehyde passed according to Kostanecki's

method (loc. cit.) via the *diacetoxy chalkone dibromide* into 7-(β hydroxy-ethoxy)-4 methoxy-flavone, and 2-2¹: dihydroxy-4 (β hydroxy-ethoxy) chalkone derived from salicylaldehyde, afforded, 2¹-hydroxy-4¹ (β acetoxy-ethoxy) flavylum chloride (IV)



(IV)

Cyclisation of the hydroxy ethyl ethers of resacetophenone, *m*-methoxy phenol and of substituted flavones with the help of anhydrous zinc chloride and phosphorous pentoxide according to the method of Rindfusz (loc. cit.) could not be accomplished and coumarane derivatives were not produced. Similarly negative results were obtained when 7- β (bromo-ethoxy)-6 bromoflavone was subjected to the action of sodium in anhydrous xylene.

T. S. W.

6—*Synthetic Production of Camphor from Pinene*. By B. G. S. ACHARYA, and T. S. WHEELER, A summary of the thesis submitted by Mr. Acharya for the M. Sc., degree of the Bombay University (July 1934), Royal Institute of Science, Bombay.

This work was undertaken to find a suitable process for the manufacture of camphor from pinene obtained from turpentine. A close search of the academic and technical literature was made and many of the proposed processes were tested in the labora-

tory with systematic control of the experimental conditions. Not only have the conditions proposed been examined, but improvements have also been made since patentees often refrain from stating the best conditions. Besides, an entirely new process has been discovered for the direct oxidation of camphene to camphor.

The technical preparation involves five stages. Pinene is converted by treatment with hydrogen chloride into pinene-hydrochloride. This on removal of hydrogen chloride yields camphene. It is then esterified with an organic acid to yield isobornyl ester, and hydrolysed by alkali when the secondary alcohol, isoborneol is obtained. This is finally oxidised to yield the ketone camphor.

Throughout the work the ne-

cessity of using cheap chemicals has been kept in mind, and the possibilities of replacing chemicals given in patents by cheaper reagents of the same type have been systematically investigated.

B. G. S. A.

7.—*Bromination of esters containing two Aromatic Nuclei*

By G. V. JADHAV and Y. I. RANGWALA. A summary of the thesis submitted by Mr. Rangwala for the M.Sc. degree of the Bombay University (July 1934). Royal Institute of Science, Bombay.

The work is divided into two parts:

PART I treats of the bromination of cresyl and nitro-phenyl esters of benzoic acid. The constitution of bromo-cresyl esters which was left undetermined by Kauschke (J. Pr. 1895, (2), 51, 213) has been fixed by hydrolysis and synthesis. In these esters, bromine enters in the cresyl nucleus giving mono-bromo compounds while in nitro-phenyl esters, it enters in the unsubstituted acid nucleus giving mono- and dibromo-compounds. The deactivating effect of the $-\text{NO}_2$ group on these esters is strong, as a powerful carrier, namely, fuming nitric acid (sp. gr. 1.45), is required to bring about the bromination.

PART II treats of the bromination of phenyl and cresyl

esters of m- and p-nitro benzoic acids. With simple phenyl esters, only mono-bromo compounds are obtained. With the cresyl-esters mono-, di-, and tri-bromo compounds are obtained. In all these cases bromine always enters in the phenyl and the cresyl nuclei, showing thereby a complete deactivating effect of the $-\text{NO}_2$ group on the acid nucleus. The constitution of these bromo-esters is determined by hydrolysis and synthesis.

The following compounds were obtained in this investigation:—

4-bromo-2-methyl- and 4-bromo-3-methyl-phenyl benzoates; 2-bromo-4-methyl-phenyl benzoate; o-nitro-, m-nitro-, and p-nitro-phenyl-m-bromo-benzoates; o-nitro-, m-nitro-, and p-nitro-phenyl-2:5 dibromo-benzoates; p-bromo-phenyl-p-nitro-benzoate; p-bromo-o-cresyl- and p-bromo-m-cresyl-p-nitro benzoates; 4:5 dibromo-o-cresyl-p-nitro-benzoate; 3:5 dibromo-p-cresyl-p-nitro-benzoate; 3:5:6 tribromo-p-cresyl-p-nitro-benzoate; p-bromo-phenyl-m-nitro-benzoate; 4:5-dibromo-o-cresyl-m-nitro-benzoate; 3:5:6 tribromo-o-cresyl-m-nitro-benzoate; 4:6-dibromo-o-cresyl- and 2:6-dibromo-p-cresyl-p-nitro-benzoates; and 2:3:6 tribromo-p-cresyl-p-nitro-benzoate.

Y. I. R.

8.—*Suitability of some Indian Bauxites for the Production of*

Alumina. By M. S. PATEL AND G. K. OGALÉ. A summary of the thesis submitted by Mr. Ogale for the M. Sc. degree of the Bombay University (Feb. 1935), Royal Institute of Science, Bombay.

The investigation was undertaken to furnish the data necessary to work out a scheme for the manufacture of alumina from Indian bauxite.

Samples of bauxite from various places were collected and analysed. The results show that bauxite rich in alumina occurs at Radhanagari and Tungar (Bombay Presidency) and at Tikaria and Katni (Central Provinces). Their titanium content is also very high.

Attempts to find out a suitable concentration of either HCl or H_2SO_4 to remove the iron present in bauxite without dissolving the alumina resulted in failure.

Digestion of bauxite with a caustic soda solution of sp. gr. 1.42 under pressure at $160^\circ C$ for 6 hours was found to be most suitable for the determination of alkali-soluble alumina.

Fusion with sodium carbonate at $900^\circ C$ for one hour also gave nearly the same results as the alkali digestion.

Samples of bauxite containing a high percentage of alkali-soluble alumina were subjected to Bayer's process and the yield of alumina

and the alkali used up during the treatment were determined. It was found that bauxite from Radhanagari, Tungar and Katni is quite suitable for the production of alumina by this process.

The residues, obtained after treating the various samples of bauxite, were found to contain 20 to 36% TiO_2 calculated on dry basis. This high titanium content may prove of great value to the Indian aluminium Industry.

G. K. O.

9.—C-Alkyl Resorcinols:—Synthesis of Polyalkyl Resorcinols.

By R. C. SHAH and P. R. MEHTA.—A summary of the thesis submitted by Mr. P. R. Mehta in May 1935 for the M.Sc. degree of the Bombay University, from the Royal Institute of Science Bombay.

C-Alkyl phenols and particularly C-alkyl resorcinols have assumed great importance since the classical researches of Johnson and Lane (J. Amer. Chem. Soc., 1921, 43, 3487) and Dohme, Cox and Miller (ibid, 1926, 48, 1688), which culminated in the discovery of 4-n-hexyl resorcinol a valuable internal urinary antiseptic. In addition, C-alkyl resorcinol compounds have an interest of their own in organic chemistry, as some of them or their derivatives have been obtained by the degradation of important natural products.

A number of differently substituted C-alkyl monohydric phenols have been prepared by various workers to study their antiseptic action. Similar investigations have been carried out also in the resorcinol series.

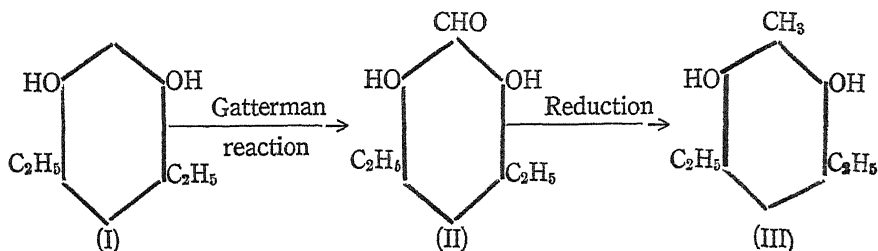
The influence of two alkyl groups in the resorcinol molecule on the antiseptic activity have been studied by Klarmann (J. Amer. Chem. Soc., 1926, 48, 2358), who has synthesized 4:6-dialkyl resorcinols.

As no work appeared to have been done upon polyalkyl resorcinols containing more than two alkyl groups, the present work was undertaken, with the object of synthesising typical polyalkyl resorcinols containing more than two C-alkyl groups, which could thus be made available, for a study of the influence of more than two alkyl groups on the

(page 109).

An interesting observation has been made that 4:6-diethyl resorcinol (I) does not undergo the Höesch condensation with acetonitrile to give the 2-acetyl compound. However it readily undergoes the Gattermann reaction and yields the corresponding 2-formyl compound namely 2:6-dihydroxy-3:5-diethyl benzaldehyde (II), converted by reduction into 4:6-diethyl-2-methyl resorcinol (III)

The orthohydroxyaldehyde structure of the aldehyde has been confirmed. (1) Knoevenagel condensation with malonic ester afforded the 3-carboxy coumarin derivative; this Knoevenagel reaction appears to have been little used by the previous workers, as a characteristic reaction of orthohydroxyaldehydes. (2) Condensation with 5:6-dimethoxy



antiseptic activity and to study as far as possible, the properties, particularly chemical, of these highly alkylated resorcinols.

4:6-diethylresorcinol was synthesised and its various reactions were studied which are described in the original paper on 4:6-diethyl resorcinol in this volume

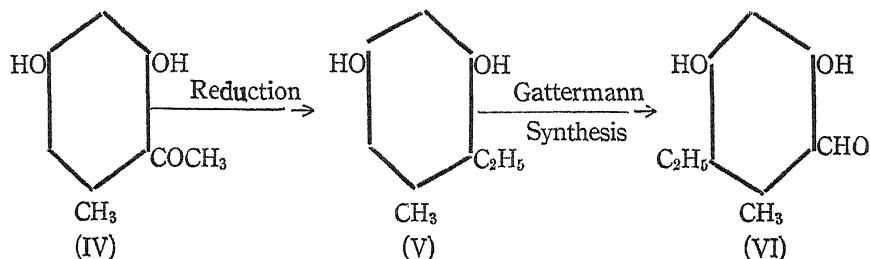
-1-hydrindone by the Perkin-Robinson method, gave a deeply coloured, well crystallised pyrylium salt. This aldehyde is of interest as it is a Y-resorcyaldehyde, only two of which type appear to be known.

Orsactophenone (IV) was reduced to 4 ethyl-5-methyl resor-

cinol (V) according to Robinson and Shah (J., 1934, 1498). This phenol was mercurated and also condensed with malic acid and aceto acetic ester and the corresponding coumarins were obtained. The Gattermann reaction gave 6-methyl-5-ethyl-2:4-dihydroxy benzaldehyde (VI)

The orthohydroxy aldehyde

edly, an interesting pyrylium salt (VII) which is probably formed from the expected 3-acetyl coumarin initially obtained, by further condensation with a second molecule of the orthohydroxy benzaldehyde. This pyrylium compound shows interesting properties and is of importance as such compounds appear to have

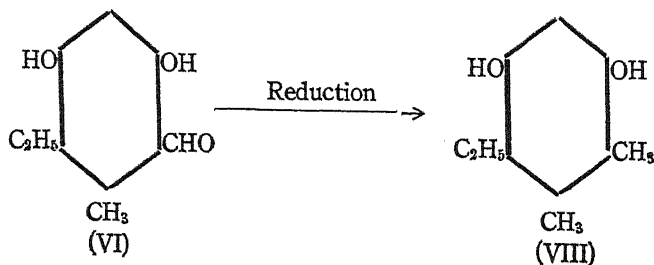
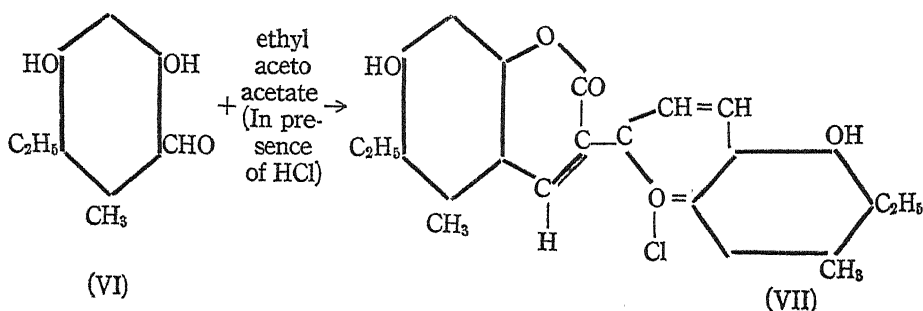


structure was proved as before.

(1) The aldehyde gave with 5:6-dimethoxy -1-hydrindone, the characteristic pyrylium salt:
(2) The Knoevenagel condensation with malonic ester gave the expected 3-carboxy coumarin.

been very little studied, perhaps the only recorded observation being, by Le Févere (J., 1934, 450) who has obtained such a compound by condensation of salicylaldehyde and ethylacetoacetate in the presence of hydrogen chloride. Reduction of the aldehyde finally gave 4-ethyl 5:6 dimethyl resorcinol (VIII).

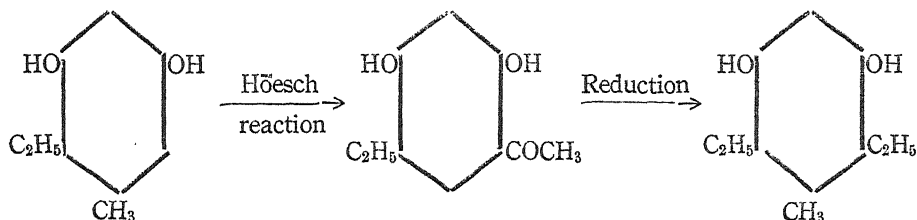
An analogous reaction with acetoacetic ester gave unexpected



4—ethyl—5—methyl resorcinol (V) by the method of Höesch, gave the ketone, 5—ethyl—6—methyl—2 : 4—dihydroxyacetophenone (IX). This when reduced by Clemmensen method gave 4:6—diethyl—5—methyl resorcinol (X).

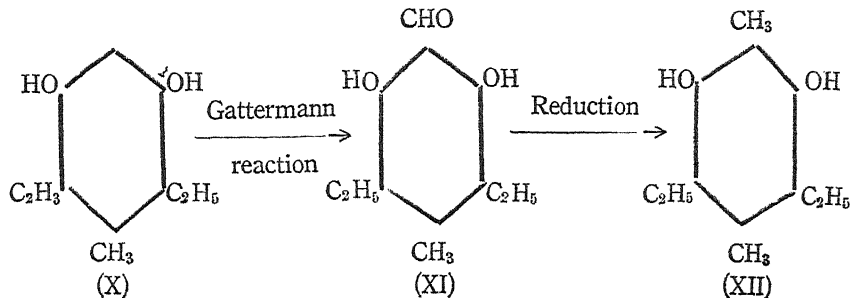
—dimethoxy—1—hydrindone by the Perkin—Robinson method.

Reduction of the aldehyde in the usual way afforded, 4:6—diethyl—2 : 5—dimethyl resorcinol, a tetra-alkyl resorcinol (XII). This compound is of unusual interest, as it is the first tetra-alkyl



The corresponding 5—hydroxy coumerin derivatives were prepared as usual by Pechmann reaction with malic acid and acetoacetic ester.

resorcinol to be synthesised. It is relatively very unstable and turns into a brown pasty mass spontaneously on standing.



4 : 6—diethyl—5—methyl resorcinol (X) underwent the Gattermann reaction, giving 3 : 5—diethyl—4—methyl 2 : 6—dihydroxy benzaldehyde (XI), a Y—resorcyraldehyde. As expected it gave a 3—carbethoxy derivative with a malonic ester by the Knoevenagel method and a pyrylium salt by condensation with 5 : 6

AC

R. C. S.

10—*X-Ray Investigation of crystals of Benzoin and O-Nitrodi-phenylamine.* By MATAPRASAD and JAGDISH SHANKAR. A summary of the thesis submitted by Mr. Jagdish Shanker for the M.Sc. degree of the Bombay University (February 1935). Royal Institute of Science, Bombay.
 PART I—Benzoin.

The crystals belong to the monoclinic prismatic class and the crystals examined develop $\{100\}$ and $\{20\bar{1}\}$ faces.

Rotation photographs taken about the three axes, using copper radiations from a Shearer gas tube gave the following dimensions for the unit cell:—

$a = 19.81 \text{ \AA}$, $b = 5.434 \text{ \AA}$,
and $c = 10.55 \text{ \AA}$, $\beta = 106^\circ 50\frac{1}{2}'$
The axial ratio agrees very well with that given in Groth.

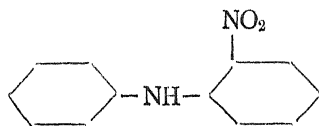
Oscillation photographs taken about the b and c axes show that (hol) planes are halved when h is odd and (010) is also halved. The crystals thus belong to the space group C_{2h}^{24} . The calculated number of molecules and that required by the space group is four showing that the molecules are asymmetric. It appears, however, that the molecules are orientated in a manner similar to dibenzyl as found by Dhar and by Robertson by X-ray methods and by Krishnan from magnetic measurements.

PART II—O-Nitrodiphenylamine

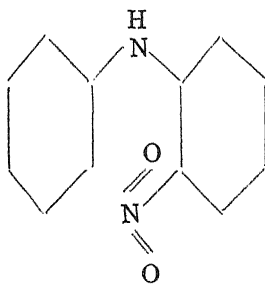
The crystals belong to the orthorhombic bipyramidal class. A direct measurement of the angles between (III) planes developed on the crystals shows that the axial ratio given in Groth is correct. The rotation photographs gave the following values for the length of the axes.

$a = 6.92 \text{ \AA}$, $b = 14.995 \text{ \AA}$
 $c = 10.32 \text{ \AA}$.

Oscillation photographs taken about a and b axes show that the crystals belong to the space group $Q_4'' \bar{10}$ with Braivais lattice. The number of molecules calculated from the dimensions of the cell and density of the crystals is four while that required by the space group is eight. This indicates that there is some symmetry in the molecules. From the chemical formula



there seems to be no likelihood of a molecular symmetry. The possibility that the crystals may belong to some other crystal class has also been thoroughly investigated, and it is found that they do not belong to any other class. The following arrangement of the rings has consequently been suggested:



M. P.

X-Ray Investigation of the Crystals of m-Azotoluene and Dibenzyl By MATA PRASAD and H. H. DALAL. A Summary of the thesis submitted by

Mr. Dalal for the M. Sc. degree of the Bombay University (August 1934), Royal Institute of Science, Bombay.

Part I—m-Azotoluene

Crystals of m-azotoluene belong to the rhombic bipyramidal class. They were examined by rotation and oscillation method using X-rays from a copper anticathode and a Shearer gas tube. The dimensions of the unit cell were found to be $a=11.8 \text{ \AA}$, $b=13.75 \text{ \AA}$, $c=7.52 \text{ \AA}$. From the reflecting planes (hol) were found to be halved when h is odd and (hko) halved when k is odd. This shows that the crystals belong to the space group Q_h^{∞} . The number of molecules in the unit cell is calculated to be four which is half the number required by the space group, indicating some molecular symmetry. Various possibilities of the arrangements of the molecules in the cell have been considered.

Part II—Dibenzyl

These crystals belong to the monoclinic prismatic class. A similar study as in Part I, gave the following dimensions for the unit cell :—

$$a = 12.7 \text{ \AA}, b = 6.11 \text{ \AA}, c = 7.61 \text{ \AA}, \beta = 114^{\circ}48'$$

In this case (hol) planes are halved when h is odd, and (010) is also halved. These halvings correspond to the space group C_{2h}^2 . The number of molecules

in the unit cell is two, while the space group requires four molecules per unit cell. This shows that the molecules have a centre of symmetry. These results agree with those obtained by Krishnan by the magnetic methods.

M. P.

Active Principles from The Fruits of Solanum Xanthocarpum. By I. Z. SAIYED and D. D. KANGA (A summary of the thesis submitted by Mr. I. Z. Saiyed for the M. Sc. degree of the Bombay University, (May 1935). M. R. S. Institute, Gujarat College, Ahmedabad and Royal Institute of Science, Bombay.

Solanum Xanthocarpum known as Bhoringani in Gujarati, Bhutkatya or Bhumiringani in Hindi, Kanteringani in Marathi, etc. is well-known in Hindu Medicine as its roots are one of the constituents of 'Dashmul Ashava.' This plant grows abundantly in India in wild state, particularly in Deccan round about the Malabar coast and in Punjab. The stems are greenish grey in colour, round in shape, and with innumerable spines. The flowers are bright blue in colour. The berries are spherical of the size of a large gooseberry, very smooth, and drooping; when immature they are green, interspersed with white bands, but when they are ripe they are of different shades of yellow only.

In Hindu Medicine the plant is described as aperient, pungent, bitter, digestive, alterative and astringent; useful in fever, cough, asthma, costiveness, and heart diseases. The stems, flowers and fruits, according to Dr. Wilson (Calcutta Med. Phys. Trans. Vol. II, pp.406) are bitter and carminative, and are prescribed in those forms of ignipetiditis which are attended with a vesicular and watery eruption. Fumigation with the vapour of the burning seeds of the plant is in high repute in the cure of tooth-ache. In the Konkan two tolas of the juice of the fresh plant with two tolas of Hemidesmus juice are given in whey as a diuretic, and the root with the chiretta and ginger is given in decoction as a febrifuge. The root beaten up and mixed with wine is given to check vomiting. The juice of the berries is useful in sore throat. In the Punjab Hills the juice of the plant is administered with black pepper in rheumatism. A decoction of the plant is used in gonorrhoea. It is also thought to promote conception in the female. Fine powder of the fruits of this plant with honey is used for chronic coughs in children (A Treatise on Vegetable Materia Medica, Part II, by Vaidya Bapalal G. Shah).

The plant under investigation belongs to the natural order Solanaceae. Of the two classes of the alkaloids which have been isolated from some of the plants belonging to this order, one class

gives alkaloids uncombined with sugars, such as the three best known alkaloids, atropine, hyoscyamine, and hyoscyne, while the other class gives alkaloids combined with sugars and are known as gluco-alkaloids.

A study of the literature on the subject of gluco-alkaloids shows that the composition of not a single solanine or its hydrolysed product, with the solitary exception of *Solanum Augustifolium* (Tutin and Clewer, J. C. S. 1914. T, 559) has been definitely established.

Dymock (Pharmacographia Indica, II, pp. 559) states that the fruits of *Solanum Xanthocarpum* were found on analysis to give alkaloidal reactions corresponding to solanine. The dried leaves gave 29.7 % ash and contained a trace of an alkaloid and an astringent organic acid giving green precipitate with ferric chloride.

G. Pendse and S. Pendse Indian J. Med. Research, 20, 663—70, 1932) describe an alkaloid in the plant (plant complete with berries) which they say is present in very small quantities. They attribute the physiological activity of the whole plant to potassium nitrate which is present in it to the extent of 1.6 %.

The present authors undertook the investigation of the fruits of *Solanum Xanthocarpum* with a view to isolate the active principle or principles from the drug, to determine their composition and

then to have their pharmacological action investigated. Three crystalline compounds have been isolated and their composition determined. They are, a gluco-alkaloid, an alkaloid and a sterol. The gluco-alkaloid which has been given the formula $C_{44}H_{78}O_{19}N$ or $C_{44}H_{76}O_{19}N$ is termed 'Solancarpine'. The alkaloid which has been given the formula $C_{26}H_{44}O_3N$ is termed 'Solancarpidine'. The sterol which has been given the formula $C_{36}H_{54}O_4$ is termed 'Carpesterol'. The products of hydrolysis of the gluco-alkaloid have been found to be the alkaloid (shown above) and glucose, rhamnose and a hexose probably galactose. There is also obtained an inorganic mineral salt which was identified as potassium chloride.

EXPERIMENTAL

The fruits of the drug under investigation were locally purchased and coarse powder prepared from them. Small portions of this material were then subjected to some preliminary tests when indications were obtained of the presence of an alkaloid, reducing sugar and an inorganic salt, potassium chloride.

For the purpose of complete examination 40 lbs. of the material were successively extracted with petroleum ether and alcohol in a large copper soxhlet.

PETROLEUM ETHER EXTRACT

After the removal of the greater

portion of the solvent, the extract yielded a solid crystalline substance, and on further evaporation, an oil. The solid substance was crystallised from boiling alcohol, when it gave the melting point $248^{\circ}C$. On analysis it gave the following result :—

C, 78.86 and H, 9.4. $C_{36}H_{54}O_4$ requires C, 78.54 and H, 9.81.

This substance showed colour reactions characteristic of phytoosterols and formed an acetyl derivative, which gave the following result on combustion :—

C, 77.09 and H, 10.13, $C_{38}H_{56}O_5$ requires C, 77.03 and H, 9.5.

This result showed the presence of one —OH group. Hence the substance has been designated 'Carpesterol' with reference to the source from which it has been isolated.

ALCOHOLIC EXTRACT

After removing the solvent by distillation, the extract was dried and treated as under :—

It was first treated with water, which dissolved the greater portion of the extract. The insoluble portion was then treated with dilute acid. It also dissolved some of the extract (acid solution). The extract which was insoluble in both of the above mentioned solvents was dissolved by dilute alkali (alkaline solution).

(1) *Aqueous Solution* : This solution was clarified with neutral lead acetate etc. and the basic

which threatened the disruption of civilisation. We had suggested then a fuller and completer development of human nature, an all-round development of the human personality, by the study of courses which would emphasise not only one aspect of human nature viz. intellectual, but also the others which are neglected at present viz. emotional and spiritual and in the introduction of which the Universities should not lag behind. A lop-sided development of human nature, either intellectual or emotional cannot take a most comprehensive view of the world situation.

Everyone who studies the world events is painfully conscious of the fact that the peace which the League of Nations is trying to establish in the world is receding further and further for the simple reason that the principal members of the League act on principles which are fundamentally opposed to those of the League. They go on increasing their aeroplanes and submarines, tanks and dreadnaughts and strengthening their land, water and air forces ; they do so because of mutual suspicions, jealousies ; no nation trusts another nation.

It would be absurd to expect an individual who has not attained peace by harmonising his thoughts, feelings and actions, in whom there is conflict, discord and disharmony, to talk of peace ; it would be folly to expect such a person to spread ideas of peace and goodwill. Equally absurd and foolish it would be to expect one nation or the League of Nations to establish peace in the world as long as they are guided by persons, who have not attained the inner peace and harmony which are characteristics of men who have gained a mastery over their lower desires and thoughts, who have brought about an alignment between their thinkings and doings and who always think and speak and act in terms of humanity, who are self-effacing, who always think of sharing their best with others, who use the power they wield, not only for the advancement of their own country but also for the advancement of other countries and who, while thinking of the interests of their own countrymen, also think of the interests of the people of other countries.

It is true the knotty economic and political problems facing the world to-day are not easy of solution ; difficult and complex they are but not impossible of solution. The best intellects of the world inspired with the highest motives must be brought to bear on them if they are to be solved at all. While we have offered some adverse criticisms against the League of Nations we cannot help mentioning that if there is at present any international body in the world which has for its aim the establishment of peaceful and harmonious relations between nation and nation and which is to act as an arbiter when there is a difference of opinion, it is the League of Nations, but if the work of

the League is to be made effective it must have the *power* to enforce its will and decisions and that its work should be above the slightest shadow of suspicion.

What part could the Universities of the world take in the solution of these problems? These problems would never be solved as long as every boy and girl is taught at home and at school that the interests of his or her country are above those of any other country in the world. The problems will be nearer solution only when every boy and girl is taught that he and she are members of one world-nation and one human family. To bring about this desirable change in the outlook of the youths every University should see that any system of education which inculcates narrow notions of nationality is completely overhauled and secondly it should see that every alumnus receiving education under its portals receives such education that it brings about an all-round development of his nature.

The world is governed by ideas and if we wish to bring about this much-to-be-desired orientation in the world's thought then we should see that we give every possible support to the League of Nations and strengthen the world opinion in its favour and also of other bodies, and there are several, which have for their aim the establishment of peace and that every boy and girl grows up in the atmosphere of this changed mental outlook.

II

A great cataclysm like the one which the unfortunate people at Quetta recently went through naturally awakens in our mind a good many thoughts. The first and foremost is the thought that science was not able to predict the occurrence of such a sudden overwhelming catastrophe as that of the earthquake which we recently had at Quetta. The scientists have to make an honest and humble confession of their inability to predict and consequently warn the people in time of the impending danger. Had it been possible to do so, there would not have been such a heavy loss of precious life. Mighty reactions and changes on a gigantic scale must be taking place in the bowels of the earth some time before the actual occurrence of such cataclysms. Is it not possible to devise sensitive instruments which would give an indication of these changes? There is ample room for research in this direction.

The second thought which presses itself upon us is whether there is any design in the occurrence of such cataclysms. The book entitled "The Great Design: Order and Intelligence in Nature" edited by Frances Mason with a valuable introduction by Sir J. Arthur Thomson published in 1934, answers this question in the affirmative. The study

of the book, which contains a collection of monographs by fourteen men of international reputation, each an expert in his own branch of science, reveals an important point that evolution is not, as was hitherto supposed, 'the result of a fortuitous concourse of atoms' but that there is ordered harmony, mathematical precision and a great design and consequently a Purposive and Directing mind behind the great drama of creation. If that is the case, then the recent convulsion and cataclysm as well as many others which the Earth has experienced in its long past history were 'part of Nature's mechanism for readjusting the earth's surface to the requirements of racial evolution.' Is there a connection between the occurrence of earthquakes and the appearance or birth of new races? Mighty upheavals have taken place in the past; titanic forces which are at work in the womb of the earth have several times brought about a redistribution of land and water on the surface of the earth, a change of climates etc. Continents have been submerged and waters of the ocean are now rolling over them. New continents have emerged where formerly there were seas and oceans. Are the islands in mid-oceans tops of the highest mountains which once raised their proud heads on the continents now submerged as revealed by the nature of vegetation formed on them? How far is the supposition true that the old earth becomes exhausted by the multitude of men and animals fed upon it and so needs renovation so that it may become virgin once again and become a befitting abode for a new race, a new and suitable home for a new civilisation? These are some of the questions which naturally arise in one's mind on the occurrence of a great cataclysm like the one we had at Quetta and which it would be worthwhile our scientists,—particularly our meteorologists and ethnologists, palæontologists, geologists and biologists—to think over and ponder, investigate and solve.

D. D. K.

III

We had referred in one of our past issues (P. 363, Vol. II, Part II) to the necessity of procuring pure wholesome food for the maintenance of the health of the people. The large number of prosecutions by the Health Department, Bombay Municipality show to what a great extent ghee and butter are adulterated. The result of these prosecutions was not as satisfactory as was expected, for the simple reason that the miscreants were let off with easy fines. The punishment was not commensurate with the gravity of the offence. We would suggest that all cases of tampering with the purity and wholesomeness of food by adulteration should be sent for trial to one of the following officers, who realising the gravity of the offence, would give exemplary punishment to the offenders,

namely, the Principal of the Royal Institute of Science, the Deans of the two Medical Colleges, the Deans of the Faculties of Science and Medicine. It should be noted in this connection that the manufacturers of adulterated ghee, butter, other foodstuffs and medicines should be considered as greater offenders than the sellers; they should be found out and hauled up before the Magistrate. It is only in this way that the Health Department may be enabled to bring this mal-practice under control and eradicate it in the near future.

D. D. K.

Reviews

THE TWENTY-SIXTH ANNUAL REPORT—THE INDIAN INSTITUTE OF SCIENCE, 1934-35

We have received a copy of the twenty-sixth annual report of the Council of the Indian Institute of Science for the Session 1934-35 which makes a very interesting and instructive reading. The Director and Staff deserve to be congratulated on the fine results obtained as shown by the large number of original publications from the different departments during the year under report. The newly-opened Physics Department, in spite of many difficulties, had 39 original papers to its credit; the Department of Chemistry (General and Organic) 23 between its two divisions; the department of Biochemistry 49 and the department of Electrical Technology 15, making a total of 126 papers which is undoubtedly a fine achievement.

The total income for the year under report was Rs. 5,45,624. The expenditure for the same period was Rs. 6,57,941, showing an excess of Rs. 1,12,317 over the income. The total number of students during the year under report was 181 of which the Department of Electrical Technology claimed 50 per cent. and the departments of Chemistry, Biochemistry and Physics 22, 16, and 11 per cent. respectively. The expenditure per student thus comes to Rs. 3635 per year. This may seem to be a big figure to a layman and naturally lead him to inquire as to whether the Institute has achieved any substantial results during its existence of 26 years commensurate with the sum it spends per each student per year and whether it has been able to implement its declared policy and justify the hope of its large-hearted and far-sighted donor, the late Mr. Jamshedji Nusserwanji Tata and to find out how far the researches carried out in the Institute during the last quarter of a century have gone to help, directly or indirectly, industry, or science (pure and applied), or both. A report of the Institute of the last 25 years treated from this point of view and including a comparative statement of expenditure per student per year of other Research Institutions of a similar kind in other parts of the world would be helpful and illuminating.

The excess of expenditure over income by Rs. 1,12,317 during the year under report does not show a sound financial position of the Institute; in this connection the recommendations of the Economic

Committee appointed by the Council will go a long way to stabilise the financial position of the Institute and we are glad to find a saving of Rs. 20,000 in recurring expenditure in the budget of 1935-36 as compared with the budget for 1934-35. The other recommendations of the Economic Committee were "the promotion of the newly opened Department of Physics, the foundation of a Chair of Mathematical Physics and the development of the Central Workshop as a centre of Mechanical Engineering and industrial Research." We are of opinion that if the name "central Workshop" be expanded to "central Workshop and Department of Applied Chemistry" and if it is made to include "Chemical Engineering" as well, it would catch the imagination of the commercial people and industrial magnets and induce them to give large sums of money ear-marked for some specific industrial research.

This review would not be complete without reference to a significant event which occurred during the year, namely, the foundation of the Indian Academy of Sciences which will play an increasingly important part in the advancement of Science in India. It has begun well, shows great vigour and is filling an important gap in the scientific life of the country under the able presidentship of Sir C. V. Raman who is also the Director of the Institute.

D. D. K.

REPORT OF THE ROYAL INSTITUTE OF SCIENCE, 1926-34

The copy of the Second Report of the Royal Institute of Science, Bombay for the period 1926-34 which we have received for review affords an interesting reading. It shows an all round progress in all the departments of the Institute and the Principal and members of the teaching staff deserve to be congratulated on their fine achievements. Taking into consideration the number of the undergraduate and post-graduate students in the year 1933-34 and the accommodation available it seems the Institute has been working to its maximum capacity and if the same rate of increase in the number of post-graduates continues the Principal will be faced with the difficult question of finding out further accommodation for the increasing number of post-graduates seeking admission to the Institute. Government will have to tackle this problem sooner or later, sooner rather than later and will have seriously to consider the question of relieving the Royal Institute of Science of a major part of its undergraduate teaching, namely F. Y. A. Physics and I. Sc. courses, if not the whole of it, to begin with.

The contract grant fixed for the year 1934-35 was Rs. 32,500, the average of the last three years being Rs. 32,830. The expenditure per student per year in the year 1932-33 was Rs. 608. The total number of papers published during the period under review (1926-1934, 1st quarter) was 128 and the total number of approved M. Sc. theses for the same period came to 96; the total number of researches in progress in 1933-34 was 101. Thus the report shows that a considerable progress has been made during the period under review to develop the Institute into a centre of post-graduate work and research in science. To make further progress in the same direction it will be necessary, as the Report observes, (1) gradually to discontinue the undergraduate teaching which takes up at present 50 per cent. of the space of the Institute, (2) to create a number of bursaries so that the holder may become self-supporting and work after taking the M. Sc. degree for the Ph. D. and D. Sc. degrees of the Bombay University. Research of the high quality can be carried out only with the aid of such trained students; (3) to increase the staff, the equipment, and the grants of the Institute. It would be desirable to have a graded staff with an assistant Professor and a Lecturer added to the existing cadre in each department; (4) to promote in every possible manner the prosecution of original research work of a high order by the staff and students. To carry out these objects what is required is money.

Scientific research is the life blood of every industry; the prosperity of an industry depends upon the development of scientific research and encouragement and financial help given to it. This link between science and research on one hand and industry on the other requires to be forged. In other words the public in general and the industrialists in particular require to be *educated* by lectures illustrated with slides and cinema films, by opening museums, by practical demonstrations and by showing them what the other countries are doing in this direction. The Royal Institute of Science with its highly qualified staff is the best body to forge this link. The newly opened Department of Chemical Technology may join hands with the Royal Institute of Science in this matter and both together may carry on vigorous propaganda in the two chief industrial centres of the Presidency, namely, Bombay and Ahmedabad and convince the industrialists that they stand to gain by any help which they might give for research in the form of donations, scholarships etc. We would earnestly appeal both to Government and industrialists to give generously if they wish to see the Royal Institute of Science take its rightful place in the life, industry and culture of the Presidency.

D. D. K.

Junior Trigonometry for Colleges, By MESSRS. K. S. PATRACHARI, M. A., L. T. and S. A. MANI, M. A., L. T. (Longmans, Green & Co., Ltd. Price Rs. 2/-)

It would not be fair to look for originality in a college text-book, especially in a subject like Trigonometry where so many text-books have appeared that not only the book-work but the examples too have become standardised. We may, however, expect a thorough presentation in any mathematical book coming from Kumbakonam, the fountain head of Indian Mathematics and we find it in the *Junior Trigonometry for colleges* by Professors Patrachari and Mani of the Government College, Kumbakonam. The book is handy, well printed and illustrated with neat figures and may be recommended as a text for the Intermediate stage. It also contains a number of solved examples, to illustrate methods of solution, but one wonders if a solution like that of ex. 17 on p. 18 is really helpful to the student. Thus in solving the equation $2 \cos^3 \theta + \sin^2 \theta = \cos \theta$ one would naturally proceed to change $\sin^2 \theta$ into $1 - \cos^2 \theta$ thus giving a cubic equation in $\cos \theta$; instead of which, the terms in $\cos \theta$ are first collected together and factorised, and as the factor $1 - \cos^2 \theta$ happens to be conveniently present, that is changed into $\sin^2 \theta$. So the solution appears to depend more on good luck than on any systematic attempt on the part of the student.

We may also question the remark on p. 29 viz. "When we say that $\sin \theta^0 = 0$, we do not mean that the sine of a zero angle is zero. Such a statement would be absurd, because a zero angle will mean an angle which is non-existent, and when there is no angle, how can we speak of its sine? The statement is used to indicate the fact that, if an angle becomes very small, its sine also becomes very small, or more precisely, the sine of an angle can be made to differ from zero by as small a quantity as we please, by taking a sufficiently small angle."

Has a zero angle then no business to exist in its own right, but only as a limiting case?

However these are minor blemishes which do not detract from the merits of this useful book.

Relativity By F. W. LANCHESTER LL. D., F. R. S. (Constable & Co. Ltd. pp. xii & 222; price 12/-).

We have here an interesting little volume by the famous auto and aero engineer, Dr. Lanchester, proposing to give "an elementary explanation of the space-time relations as established by Minkowski and a discussion of gravitational theory based thereon."

In part I which consists of 5 chapters, a discussion of the special theory of relativity is given. The author shows great respect to Minkowski's synthesis of space-time but curiously enough is suspicious of Einstein's philosophy on which it is based. He gives an elementary derivation of the Lorentz transformation from the postulate of the constancy of the velocity of light for all observers but doubts if the velocity of light is actually the boundary velocity. Again by defining the *cosmic velocity* of a particle to be $\log \frac{(c + v)}{(c - v)} \frac{1}{2}$, he obtains the

Newtonian law for the addition of *cosmic* velocities and regards the mass of a particle as independent of its velocity ; and so on.

Part II is wholly original. The author is not satisfied with Einstein's general theory of relativity and modifies the classical theory of gravitation by supposing the orbits of the planets to be subject to the Fitzgerald contractions appropriate to their velocities. The amount of "deficiency" for circular orbits thus comes out to be about 3 miles for every planet of the solar system. It moreover explains the bending of light in the Sun's gravitational field as given by Einstein's theory. But the author is modest enough to state that he is not satisfied with even his own theory, which "lacks finality" and in which "there is a certain want of cohesion." In the concluding chapters the author similarly criticises the conceptions of spherical or other types of universe, arising from "the equations of the mathematicians or rather from the faulty interpretation put upon them." He does not think, however, "that we have any business to concern ourselves with theories relating to the ultimate, it savours too much of the theologian ; but in accordance with the true spirit of scientific philosophy, we should endeavour to unravel the skein from the end we hold in our hands, rather than make premature guesses or assumptions concerning the remote origin of the tangle."

There are 12 appendices, some dealing with mathematical points left out from the body of the book and other discussing relevant topics at greater length.

The book is very interesting but is not meant for a beginner who wishes to make a study of Einstein's theory. The elementary discussion moreover suffers from too much condensation. Thus the aim of §19 as stated on p. 24 does not appear quite clear ; nor is it stated anywhere that fig. 4 is an elevation and not a diagram of the usual type. Similarly in §24, figures 11 and 12, to derive the Fitzgerald contraction the rod in the K system will not appear parallel to A, B, as may be deduced by the beginner. Its representation in space-time to K is the oblique trace between the parallel lines as shown, but its position at any instant (K's) is parallel to AB. When measuring it therefore

there is no reason why K should allow it to slide along his own measuring rod as suggested in 28. These and other points require to be made clear.

The book is well printed and illustrated. Some diagrams are repeated to facilitate reference without turning over a page: a useful innovation. But the price 12/- appears to be a bit too stiff.

K. R. G.

Elementary Electricity and Magnetism. By R. W. HUTCHINSON, M Sc., (University Tutorial Press) London, 1934, 6/6.

The first and the foremost aim of the writer of this book, as he puts it, has been to produce a modern elementary book suitable for junior readers—an elementary book in accordance with the science as we know it *to-day*, not as it stood thirty or more years ago. This aim has been successfully achieved. The book is made as representative of modern ideas as possible. It would be an excellent book for the I. Sc. students of this University. The experiments are chosen carefully. The demonstration of the Ampère's rule (P. 105) and the dependance of the potential on the surface of the conductor (p. 186) are really interesting and simple. The diagrams of apparatus are also plainly drawn, avoiding most of the unnecessary details. The telephone circuit (p. 405) is an excellent illustration. The book has that touch of completeness inasmuch as it finds room for accounts of the Television and the more recently known Neutrons, Dipsons and Positrons.

G. R. P.

Sound. A physical text book. By E. C. RICHARDSON, B.A., Ph.D., D.Sc. (Edward Arnold and Co., London, 1935) 2nd. Ed. 15/-.

The importance of the study of sound has increased of late. Greater attention is being paid to the subject by students and research workers in the last twenty years or so particularly on account of the extraordinary development of broadcasting and the rapid progress in the recording and reproducing apparatus employed in the talkies. It has proved once more that any particular branch of science, however academic it may look in the beginning, suddenly rises into practical eminence when it finds application in industry. Sound is one such subject. It occupies quite a different position in physics to-day than it ever did before.

AE

The book has an ambitious programme. It covers all that a student requires for a degree examination of the university, but it contains something more. It contains information which would meet the needs of the research worker and the technician by describing the important work in applied acoustics and by giving copious references to original papers.

The chapter on acoustic impedance deals with the design of acoustic filters. The information should prove useful and inspiring for anyone who is anxious to purify a note. The same could also be employed commercially, for instance, a low-pass filter in the tone-arm of a gramophone should be useful in filtering out the scratch of the needle. The same subject finds application in the designs of exhaust silencers of motor vehicles.

Much attention is devoted in this book to the recent work on supersonics. The chapters on subjective sound and technology of sound are most interesting and the reader would find enough evidence therein to convince him that sound of the present day is a subject of commercial importance.

G. R. P.

Heat. By R. W. HUTCHINSON M.Sc., (University Tutorial Press)
London, 1935, 3/6

This book deals with the elements of heat both theoretical and practical and is of a standard somewhat higher than the I. Sc. standard of this university. The subject matter is properly illustrated with numerous examples and applications from practical life.

G. R. P.

Elementary Mechanics and Hydrostatics. By F. BARRACLOUGH M. A.,
(University Tutorial Press) London. 1934, 3/6

This book is a clever attempt at writing on a mathematical topic in an interesting manner. The author holds a definite view that, whilst theory should not be neglected experiments must be performed if the subject is to be properly taught. Subjects such as these cannot be adequately dealt with in the mathematical class-room. The teacher may be a mathematician or a physicist, but his work of teaching can only be completed in a physical laboratory. The book is studded with numerous practical appliances and convincing experiments. Illustrations and examples are very carefully chosen. On page 80 there is a simple and appealing problem in graphical statics.

The Archimedes principle is explained by means of the experiment on page 121. The book can be usefully read by I. Sc. and J. B. Sc. students of this University.

G. R. P.

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‡Librarian and Editor, The Academy of Natural Sciences of Philadelphia, Nineteenth and the Parkway, Philadelphia, U. S. A.

Librarian, Division of Plant Industry, 590, Vermeulen Street, Pretoria, Transvaal.

Librarian, Kungl. Tekniska Hogskolans Bibliotek, Stockholm.

Library, League of Nations, Geneva.

Librarian, Library of Universited de Antioquia.

Librarian, The New York Academy of Medicine, 2 East 103rd Street, New York City.

Librarian, the Rice Institute, Houston, Texas, U. S. A.

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The Chief, Scientific Library Division, P. O. Box 774, Manilla P. I.

The Director of the Psychological Institute, Sendai, Japan.

*The Editor, Biological Abstracts, University of Pennsylvania, Philadelphia, U. S. A.

The Field Museum of Natural History, Roosevelt Road, and Lake Michigan, Chicago.

The Library, John Hopkins University, Baltimore, Maryland.

The Man in India, Church Road, Ranchi, Bihar and Orissa.

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*Part V for abstracting purpose only.

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NEW BOOKS ON SCIENCE

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[BIOLOGICAL SCIENCES, INCLUDING MEDICINE: NO. 4]

Vol. IV]

March, 1936

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VOL. IV]

MARCH, 1936

[PART 5

OBSERVATIONS ON SOME SPECIES OF VOLVOX FROM
POONA WITH THE DETAILED DESCRIPTION
OF VOLVOX POONAENSIS

by

V. V. APTE

FERGUSSON COLLEGE, POONA

(*With 7 Text-figures and 14 Plate figures*)

CONTENTS

Introduction,—The Volvox of Poona (1) General Characters
(2) Asexual Reproduction (3) Sexual Reproduction (4) Identification,
—Volvox dissipatrix,—Volvox prolificus,—Volvox carteri.

INTRODUCTION

Except the Volvocales from South India described by Iyengar (9) practically nothing is known about these interesting Algae from any part of India. It is, therefore, attempted in this paper to record some observations on some species of the genus Volvox collected from Poona and its neighbourhood. Two of the species described are abundantly found in Poona which is situated about 2000 feet high from the sea-level on the eastern slope of the Western Ghats. The other two species have been so far found at the hill forts Sinhgad and Purandar the heights of which from the sea-level are more than 4000 feet.

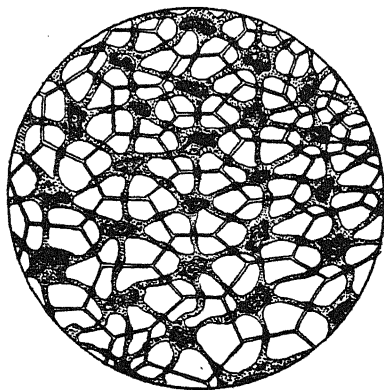
These species have been found in abundance in freshwater ponds of these places. They occur in association with water-plants like *Lemna*, *Spirogyra*, etc. They are generally confined to clear water and scarcely occur in turbid or muddy water. During and after the annual rains (July to December) they occur in most of the pools with clean water. In dry parts of the year the volvox is forced to go through a period of rest.

A NEW SPECIES OF VOLVOX FROM POONA

(1) GENERAL CHARACTERS

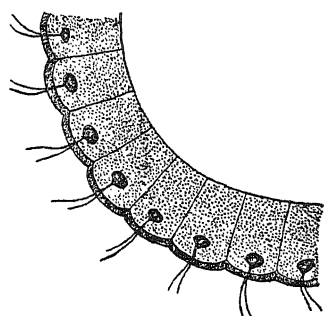
The plant appears to be encased in a colourless mucilaginous sheath which is smooth and slimy. With the help of its cilia the plant rotates about its longer axis and moves in various directions in water. The cells of the plant are very close together at its posterior part, while at the anterior they are comparatively loosely set. Though the exact distance between any two neighbouring protoplasts is not always the same, from a number of measurements on fresh material it can be said that the average distance between two protoplasts in the posterior part varies from 2μ to 3.5μ , while in the anterior part it is as much as 4μ to 5μ . The plant is slightly egg-shaped and hence the mean diameter is always measured. The diameter of a plant varies between 400μ and $1,000\mu$, while the number of cells in a plant varies between 7,000 to 10,000.

Each constituent cell of the plant is more or less pentagonal or hexagonal in outline (Text-fig 1; Plate III, fig. 7). The



Text-fig. 1—Diagrammatic surface view of
Volvox poonaensis.

diameter of the protoplast varies between 5μ and 6μ , although in some cases it is as long as 8μ . The protoplast is almost stellate in surface view on account of its giving off from its sides 5 or 6 clearly visible protoplasmic strands to the adjoining cells which in turn have similar ones to meet them. The side view of each protoplast is slightly ovate with the upper part conical and the protoplasmic strands are seen to be attached to the sides.



Texti-fig. 2—Diagrammatic lateral view of the wall of *Volvox poonaensis*.

The cell-wall (Text-fig. 2) is thick and mucilaginous being colourless and transparent. It cannot be seen in an unstained specimen which only exhibits a net-work of protoplasts connected by the communicating protoplasmic strands. In order to determine the nature of the cell-wall, stains such as Safranin or Methyleneblue, have to be used. These two stains bring out clearly the cell-wall while iodine stains the nucleus and the cell-contents fairly well. The cell-wall consists of three layers; the outer, the inner and the

middle one. The outer layer is the original cell-wall—called middle lamella; inside this is the thick mucilaginous middle layer, while the inner is thin and membranous. The thickness of the cell-wall is mainly due to the mucilage mass of the middle layer which is not uniform all-round. The cell-wall is thinnest on the peripheral surface, being perforated in the centre of the wall to allow the two cilia to come out. It is much thicker on the sides but it allows the protoplasmic strands to communicate with the adjoining cells. On the basal side, the cell-wall is thickest. Like the external envelope of the plant there is also formed the internal thick mucilaginous envelope by the united internal walls of the cells. In a stained preparation it appears to form an inner circumferential zone of the plant. Thus the radial axis of the cell exceeds the transverse one which on average varies between 10μ and 16μ . In a stained specimen the surface of the plant looks like a plate of hexagonal or pentagonal cells arranged just like the pavement of the floor.

The nucleus (Text-fig. 1) is very conspicuous and occupies the organic centre of the protoplast. At its basal part is an irregular chloroplast in which lie two or four pyrenoids. There are a few contractile vacuoles in the protoplast. A conspicuous red eye-spot is also present in the upper part of the protoplast. The eye-spot is large and prominent in the cells of the anterior end and gradually diminishes in size towards the posterior end, while in some of the posterior cells it is almost absent.

The cilia are the organs of locomotion of *Volvox*. Each cell (Text-fig. 2) has two cilia attached to it at its peripheral end. In a

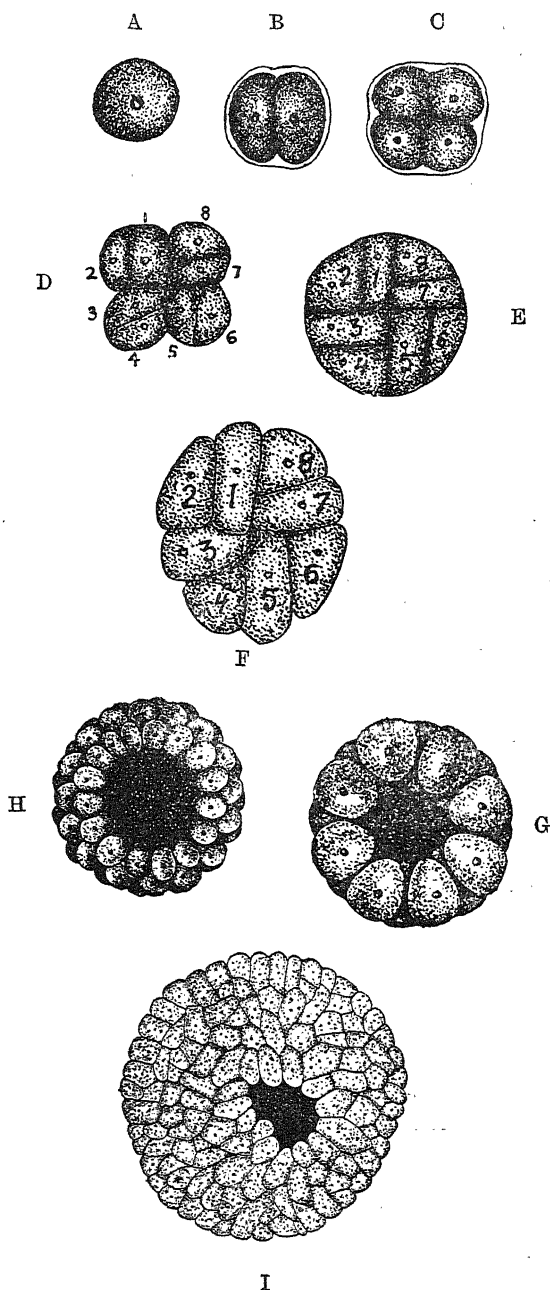
Volvox where daughter colonies or sexual reproductive bodies have been formed the cilia of the cells do not move actively but the plant as a whole remains more or less stationary. Ultimately with age the movement stops and the plant disorganises.

(2) ASEXUAL REPRODUCTION

Asexual reproduction is carried out by the formation of gonidia which finally develop into daughter colonies. This gonidial formation is generally associated with conditions suitable for luxuriant growth. Each gonidium (Text-fig. 3, A) is developed from a single vegetative cell. Many such cells are differentiated but only a few develop to form daughter colonies. Each gonidial cell first divides along its longer axis into two cells in a vertical plane; the two daughter-cells (B) again divide along its longer axis into two, the vertical plane of this division being at right angle to the previous plane of division. Thus four cells are formed (C). Each of these four cells again divides in a vertical plane into two unequal cells as the plane of division is parallel to one side of the cell and cuts the other side at a point a bit removed from the centre. This division is symmetrical in all the four cells and it results in the formation of four cells—shorter and broader and other four cells—longer and narrower (E). The former lie removed towards the circumference while the latter extend from the centre to the circumference. These longer cells meet at the centre and thus the connection of the shorter cells with the centre is cut off. The four narrow cells meeting at the centre form the well-known *Volvox*-cross, while the other cells are placed in the four angles, their angular sides being directed towards the centre.

These eight cells divide again into sixteen cells (Text-fig. 3, F). This plate of sixteen cells then becomes slightly concave and by further divisions of the peripheral cells this concavity deepens and assumes the form of a shallow cup. By further growth the mouth of the cup becomes smaller and thus a hollow daughter colony is formed with a small aperture at one end (H and I). This end is directed towards the circumference of the mother plant.

Before the daughter colony assumes the final form its hollow body is turned inside out so that the anterior ends of the cells that were first turned towards its cavity are directed towards the exterior, and the posterior ends are directed inwards. The small opening is then closed and a daughter colony is fully formed.



Text-fig. 3—Stages in the development of a gonidium. A, one-celled ; B, two-celled ; C, four-celled ; D, E and F, eight-celled stages ; G and H, later stages ; I, young colony before coming out.

The cells of the daughter colony develop cilia and with their help it is seen moving inside the mother plant. Many a times some of the cells of the daughter plant appear slightly different as they form the initials of the grand-daughter colonies. Although these rudiments are seen, actual grand daughters or the sexual reproductive bodies have not been observed in any of the daughters while still within the body of the mother.

Although many initial cells are found in a plant the number of daughter colonies is generally 8, but very often less ; rarely it is 12 or even 16. The daughter plants are in different stages of development and possibly the space inside the mother plant sets a limit to the number of daughter colonies finally formed.

With the adult daughter plants the mother plant becomes rather sluggish. It is observed that daughter colonies come out by breaking open the mother plant at different places which afterwards disorganises and dies. The average colony inside the mother plant is 250μ in diameter, but after it comes out and moves as a free plant the size is increased and it varies between 600μ and 1000μ . This increase in the size of the plant is not due to the increase in the number of cells that go to constitute it ; it is rather due to the increase in size of the individual cells. The cell-walls, which were very thin when the plant was young and inside the mother plant, gradually become thicker and thicker by the deposition of a mucilaginous substance. The protoplasts become naturally separated from one another, though they remain in communication by means of their strands. That the number of cells does not increase with the increase in size of the plant can be proved by the following calculation.

The diameter of the daughter colony is 250μ . The area of its surface is therefore $4 \times \frac{22}{7} \times 125^2$ sq. μ . The diameter of the cell varies from 5μ to 6μ . The area of the cell surface is $\frac{22}{7} \times \frac{5}{2} \times \frac{5}{2}$ when the diameter of the cell is taken as 5μ .

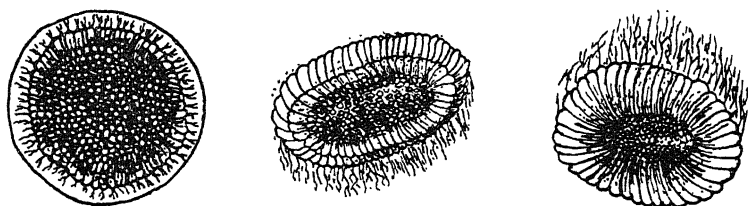
The total number of cells is therefore $\frac{4 \times \frac{22}{7} \times 125 \times 125}{\frac{22}{7} \times \frac{5}{2} \times \frac{5}{2}}$,
i.e., 10,000

If the diameter of the cell is taken as 6μ the number comes to 7,000. Thus the number of cells found in a young colony varies between 7,000 to 10,000 ; in other words, it is the same as that of the adult colony.

(3) SEXUAL REPRODUCTION

The daughter colonies of successive asexual generations gradually diminish in size. Then at the sexual phase the plant becomes considerably smaller as can be seen from its diameter which varies between 400μ to 500μ , as against 600μ to $1,000\mu$ in the vegetative phase. The shape and other characters of the colony remain the same.

The Volvox, under consideration, is monocious and protandrous¹. The sexual bodies are formed towards the posterior part (Plate II, fig. 4). There are generally 5 to 6 antheridia, rarely the number is 8. The antheridium is formed from a single cell. A vegetative cell first loses its cilia and gets bigger at the cost of the surrounding cells which on that account appear smaller. This



Text-fig. 4—Three views of the antheridium of *Volvox poonaensis*.
 $\times 820$ (approx)

formation is in no way different from that of the gonidial formation. The cell divides and subdivides and a group of cells is formed within the original cell-wall. The number of cells normally formed in an antheridium is about 128. Each cell then functions as a spermatocyte and gives rise to a sperm. The sperm is 5μ to 6μ long, greenish yellow in colour and has two cilia. These cilia are independently developed and not derived from those of the original cell.

The antheridium has the form of a flattened disc, a few cells thick, in which the sperms are so arranged that their heads point towards the centre of the disc, while their tails radiate from the rim and give the antheridium a ciliated appearance (Text-fig. 4). The antheridium is 35μ in diameter and greenish yellow in colour. The mature antheridium leaves its place as can be seen from the blank spaces in the colony. Sperms were seen moving through the matrix but the actual fertilisation was not observed.

1. Stray cases in which the plants had within its body daughter plants in various stages of development and also many oogonia or oospores have been observed.

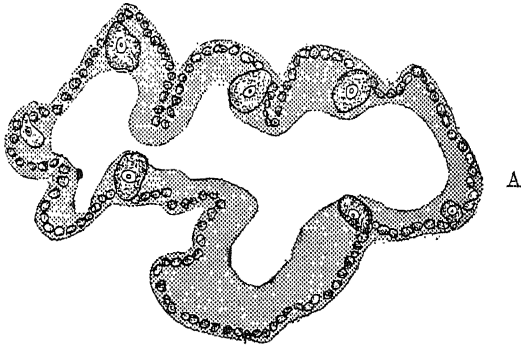
Like the antheridia the oogonia are also formed towards the posterior part of the plant. The initial cells (Text-fig. 5) lose



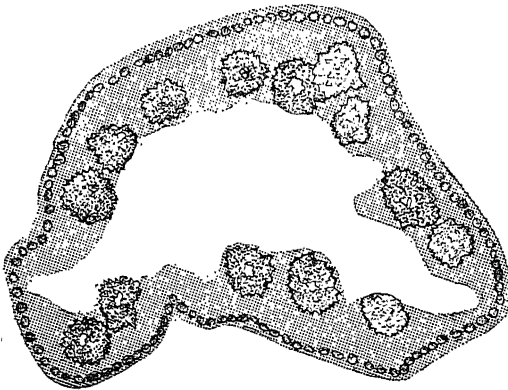
Text-fig. 5—Formation of reproductive cells in *Volvox poonaensis*.

their cilia and become very large apparently at the cost of adjoining cells. It is not unusual to find a few cells united into one large cell which then becomes an oogonium. The oogonium (Text-fig. 6 A) is pear-shaped with its apex a little drawn out and directed towards the circumference beyond which it slightly projects

while the broader base hangs down into the cavity of the



A



B

Text-fig. 6—Sections of *Volvox poonaensis* showing oogonia and oospores $\times 200$.

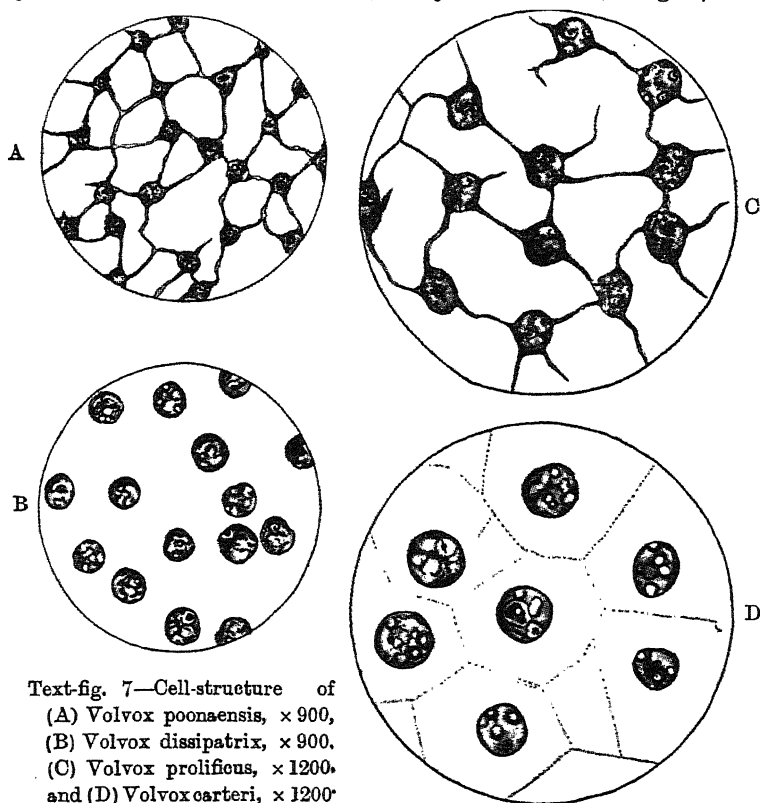
plant. The oogonium is many times the normal vegetative cell in size. Its transverse diameter often measures from 18μ to 22μ . Along with

these changes the red eye-spot disappears from the oogonium and it becomes roundish in form. There are generally 80 to 120 oogonia in a colony. This number often reaches even 200. All these female gametes lie embedded in the peripheral rim of the mucilage where they are seen even after fertilization. In the *Volvox* under consideration fertilization takes place in the circumferential zone and not in the cavity (Text-fig. 6B). More work is necessary to say exactly whether there is cross or self-fertilization.

The ripe oospore (Plate 4, fig. 8) has a thick outerwall which is beset with a number of short conical projections which are 8μ long. Such a kind of wall is called sub-stellate. The oospores are at first green but the colour soon changes to brown and then blackish. The mother colony soon decays and the free oospores sink to the bottom.

(4) IDENTIFICATION

The genus *Volvox* has been differently divided into species by different authors — Shaw, Playfair, Pascher, Engler, etc.



Without going into the merits or demerits of their bases of

classifications the writer has followed the classification given by Engler in the main, while for the specific details he has referred to Pascher's description and also to Iyengar (1933) who has described some 8 species from South India. Engler has given 17 known species of *Volvox* from all over the world. These have been placed by him into six groups. Out of these six groups only in the first the plant is possessed of thick communicating bridges while in the second these bridges are present but are hair-like and in the last four the bridges are either absent or invisible. It has already been mentioned that thick communicating bridges are present in the *Volvox* of Poona (Text-fig. 7, A) and that the inner wall of each of its cells is very distinct. It, therefore, comes under the first group namely *Euvolvox*.

Further, according to Engler six species are recognisable in this group viz. (i) *V. globator*, (ii) *V. perglobator*, (iii) *V. rousseleti*, (iv) *V. merrillii*, (v) *V. barberi* and (vi) *V. lismorensis*. The *Volvox* of Poona being homothallic can stand comparison with only those species out of these six, that are themselves homothallic and, therefore, (i) *V. globator*, (ii) *V. merrillii* and (iii) *V. barberi* are the species that are worth comparison.

| | <i>V. merrillii</i> | <i>V. globator</i> | <i>V. barberi</i> | <i>V. of Poona</i> |
|---------------------------------------|--|---|---------------------------------------|--|
| Diameter of the plant | asexual 1000 μ sexual 90 μ to 750 μ | | 1000 μ , 90 μ to 760 μ | 600 μ to 1000 μ and 400 μ to 450 μ |
| Number and size of cells | 17000, 12000 4 μ to 8 μ | 20000, 1500 to 10000 3 μ to 5 μ | 31000, 30000 3 μ to 5 μ | 10000, 7000 5 μ to 6 μ |
| Number and size of gonidia | 8 or less | 8 180 μ to 200 μ | 8 or less | 4 to 16 200 μ to 250 μ |
| Number and form of antheridia | Few Spherical | 6 to 15 Spherical | Few Spherical | 5 to 6 Flat |
| Number of oogonia | 120 | 20 to 64 but generally 30 | 224 | 80 to 120 sometimes even 200 |
| Size of oospores and length of spines | 36 μ to 42 μ 11 μ | 40 μ to 45 μ 46 μ to 56 μ | 35 μ 3.5 μ to 5.5 μ | 32 μ to 35 μ 8 μ |

A glance at the table given above will clearly show that the *Volvox* of Poona differs from the other three homothallic species mentioned above as regards its size, the number of its cells, the diameter of each cell, the number and size of gonidia, the number and form of the antheridia, the number of the oogonia, the size of the oospores, the nature and length of the spines on the oospore and such other important characters. The minimum number of cells in *V. merrillii* and in *V. barberi* exceeds the maximum number of cells in the *Volvox* of Poona. The antheridia are spherical in all the three species while they are flat and disc-like in the *Volvox* of Poona. The spines in these forms are quite dissimilar to those found in the *Volvox* of Poona and also their lengths differ. The number of oogonia in *V. merrillii* is 120. in *V. globator* commonly 30 and in *V. barberi* 224, while in the *Volvox* of Poona they are 80 to 120 and at times even 200.

As the *Volvox* of Poona differs in majority of characters from the above species, it deserves to be recognised as a distinct species and the author has called it *Volvox poonaensis*.

VOLVOX DISSIPATRIX (SHAW)

This alga was collected from the fort Sinhgad in 1934-1935. The fort has many tanks containing water throughout the year. Its colonies are ellipsoidal or slightly egg-shaped. They are either asexual or monœcious.

The asexual colonies. They are of varied size. The biggest observed was $2640\mu \times 2704\mu$. These colonies have 6 to 7 daughter colonies each measuring upto $825\mu \times 726\mu$. The number of daughter colonies varies greatly. The number is generally less than 10, but specimens are not wanting where the number is as high as 36 (Plate V, fig. 14) In the daughter colonies some cells are differentiated. These cells are more than 100 in number and hence it is safe to conclude that these are the initials of the reproductive cells, possibly of oogonia. The initials measure about 6.5μ to 9μ . The asexual colonies (Plate V, fig. 13) are also of smaller sizes, even smaller than the daughter colonies noted above. The protoplasts are roundish in outline as seen in surface view. The number of the cells in the coenobium varies between 18000 and 32000.

The size of the vegetative protoplast (Text-fig. 7, B) is from 4μ to 6μ and the distance between them varies from 4μ to 7μ . In old colony especially the distance between the cells of the anterior part is very great. It is observed that at the posterior it is from 5μ to 7μ , while at the anterior it is from 9μ to 18μ .

Professor Iyengar has noted a very important point in this form and that is the presence of thin protoplasmic strands which are only seen under very high magnification and with particular staining. In the observations taken, however, no such strands could be detected inspite of all the care taken.

The sexual colony. It is monœcious and as said above, is differentiated while it is within the mother colony. These colonies (Plate IV, fig. 12) measure from $693\mu \times 594\mu$ to $1486\mu \times 1333\mu$. The number of antheridia is from 5 to 11. They are mainly on the anterior side. Each antheridium measures about 42μ . The number of oogonia varies greatly. It is from 60 to 150 in general but in a few cases it was even more.

The oospores are characterised by their smooth wall which is double. They measure upto 38μ to 40μ (Plate IV, fig. 11).

This form of *Volvox* appears to be protogynous as in many cases along with the ripe oogonia young antheridia were seen associated in the same colony.

VOLVOX PROLIFICUS—IYENGAR

This species of *Volvox* was collected from the tanks of the fort Sinhgad and from a large water reservoir in the Purandar fort. This form was mainly identified because of Professor Iyengar's observations on the antheridia of this species. The plants are either asexual or sexual and the male and female colonies are distinct.

The asexual colonies. They are oval in outline and vary from $561\mu \times 627\mu$ to $1350\mu \times 1450\mu$ (Plate II, fig. 3). The number of its daughter colonies is generally 2 or 3 and in a few cases it may be upto 7. The size of the daughter colony about to escape is $462\mu \times 396\mu$. Occasionally a big daughter colony is found inside the male colony.

The size of the cell protoplast (Text-fig. 7, C) varies from 5μ to 7μ . The distance between two adjoining protoplasts at the posterior is about 4μ while that at the anterior is about 12μ . The protoplasmic strands are visible in fresh material but are not seen in old or preserved specimens.

Female colonies. They are also oval or slightly egg-shaped (Plate II, fig. 3). These colonies measure upto $1089\mu \times 924\mu$. The number of the oogonia is large, as in the specimens observed it was 221 and 282. This number appears to increase with the age of the colony. In some female colonies structures like antheridia were

seen, but as they were not clearly identified nothing could be said about them.

Male colonies. They can be differentiated very early from the development of antheridia. The various stages in the development of the antheridium (Plate III, fig. 5) are simultaneously observed in a colony. The male colony is big and oval or slightly egg-shaped. It has the same size as of the female colony being $1023\mu \times 891\mu$. The antheridial initial was 15μ , the two-celled 17μ and four-celled 21μ while a ripe antheridium measured from 42μ to 45μ . The antheridium is roundish and disc shaped.

Oospores. They are round and distinctly stellate (Plate IV, fig. 10). The spines are conical or slightly blunt and measure upto 9μ . The size of the oospore without spines, is about 30μ .

This form Professor Iyengar (9) has described in detail and recorded from the Madras Presidency and the writer has extended its habitat to the Bombay Presidency.

VOLVOX CARTERI (STEIN)

While the different stages of Volvox from Poona were being collected this alga was found in some small pools. To begin with the material was available in small quantity but later on abundant supplies could be had from the same locality. It was very easy to mark out this alga due to the absence of any protoplasmic strands. The material was obtained from the middle of September to the end of October only. The colonies of this plant are asexual, male and female.

Asexual colonies. They are more or less globose varying from $264\mu \times 231\mu$ to $891\mu \times 792\mu$. The number of daughter colonies is generally from 8 to 12 arranged more or less in pairs or in fours. The daughter colonies invariably show grand daughter initials. The grand daughter initials measure upto 21μ . The daughter colonies measure upto $198\mu \times 231\mu$.

The protoplasts (Text fig. 7, D) are roundish in outline as seen from the surface. The diameter of the cell is 6.7μ to 8μ . The size and the number of cells gradually diminish towards the anterior end and therefore the distance between two adjoining protoplasts is not the same all round. At the posterior end the distance between two protoplasts is 13μ while at the anterior it is as much as 22μ . There are no protoplasmic strands (Text-fig. 7, D). Even after staining protoplasmic strands could not be seen. The number of cells in a colony is between 3200 and 4500.

Sexual colonies. The sexual phase appears after the asexual phase as it was quite evident from observations made from day to day. The sexual colonies are either male or female. They first appear like the asexual colonies but later on they begin to show the development of male or female reproductive organs. In some cases some of the daughter colonies remain vegetative while others develop as male colonies (Plate I, fig. 2). This clearly shows the transformation of vegetative phase to reproductive one.

Male colonies. The size of the matured male colony inside the mother is $238\mu \times 252\mu$. This size diminished later on probably with the changes in the conditions of the habitat as in later observations the size was as small as $126\mu \times 140\mu$. The number of male colonies is nearly the same as the asexual colonies. Only in some abnormal cases the number was as high as 40. The development of the antheridium takes place while still within the mother colony. It is similar to that in other forms of *Volvox*. A single-celled antheridial initial is about 15μ , the two-celled 17μ , four-celled 19μ and the matured antheridium measures about 35μ . The antheridium is a platelet and not globoid. The whole male colony seems to be occupied by antheridia, their number being more than 75 or near about 100 (Plate III, fig. 6).

The female colonies. They are similarly developed. The size of the colonies is much larger measuring $504\mu \times 455\mu$. Later on the size was as small as $245\mu \times 210\mu$. The number of female colonies was generally 8 to 12 but in some abnormal cases it was as large as 60 in one mother colony. Each female colony has 30 to 35 oogonia (Plate I, fig. 1). The oogonia are developed from the original vegetative cells and the size of the ripe oogonial cell is 35μ .

The oospores. Their number is about 35 in each colony. The oospore (Plate IV, fig. 9) varies between 42μ and 45μ . The outer wall is wavy in outline. It can neither be called smooth nor spiny.

This alga was first described by Carter from Bombay in 1859 as *V. globator*. Later on Stein revised it and has named it *V. carteri*. Iyengar has reported it from Mylapore (Madras) (9).

ACKNOWLEDGMENTS

The author takes this opportunity to express his indebtedness to his teacher Professor D. L. Dixit of the Fergusson College, Poona, for his help. He also thanks the authorities of the Bombay University for the grant they have made towards this work.

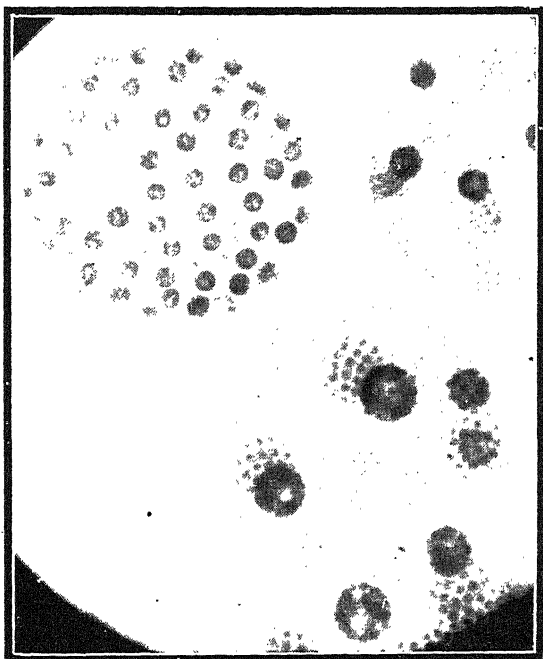


Plate I, fig. 1—Photograph of *Volvox carteri* showing large asexual and small female colonies. x80

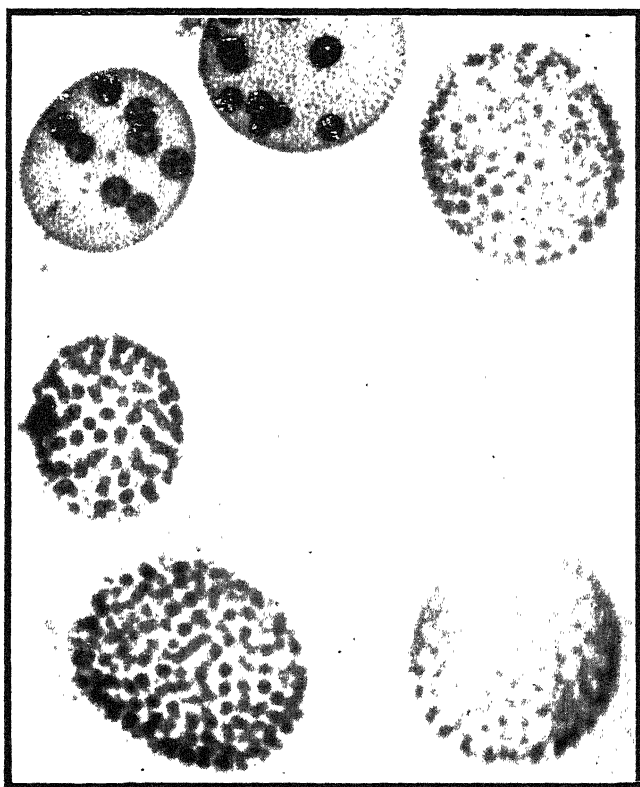


Plate I, fig. 2—Photograph of *Volvox carteri* showing two asexual and four sexual colonies. The asexual colonies show grand-daughter-initials. x140



Plate II, fig. 3—Photograph of *Volvox prolificus* showing asexual and sexual colonies. A male colony with antheridia is seen in the centre, x50

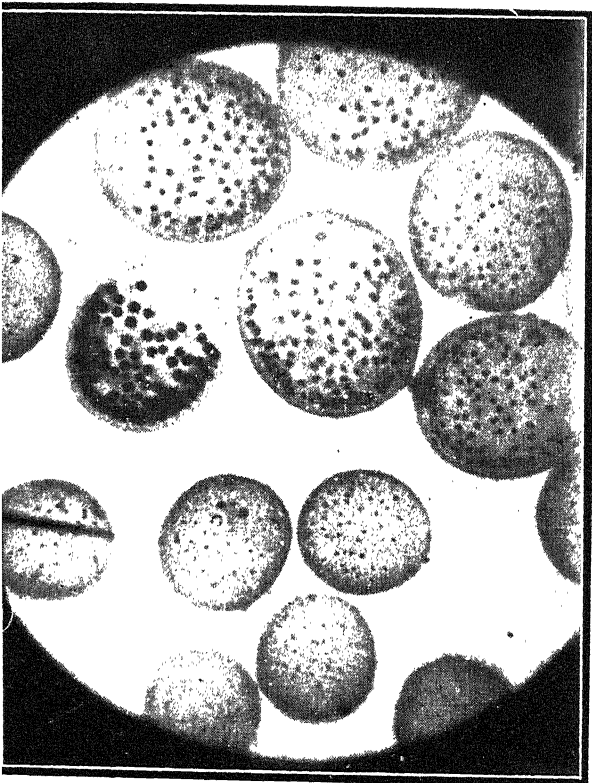


Plate II, fig. 4—Photograph of *Volvox poonaensis* showing sexual colonies. Pointer showing an antheridium, x60

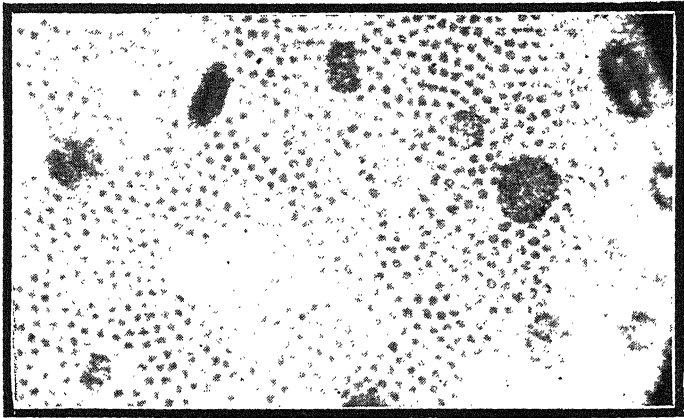


Plate III fig. 5—Photograph of a male colony of *Volvox prolificus* showing different stages of developing antheridia. x250

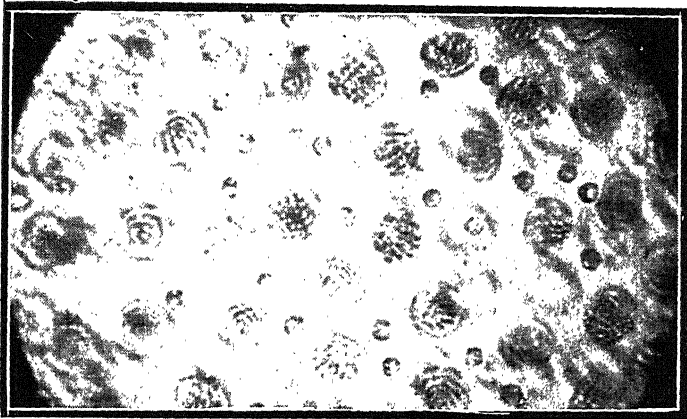


Plate III fig. 6—Photograph showing a male colony of *Volvox carteri* containing many antheridia. x250

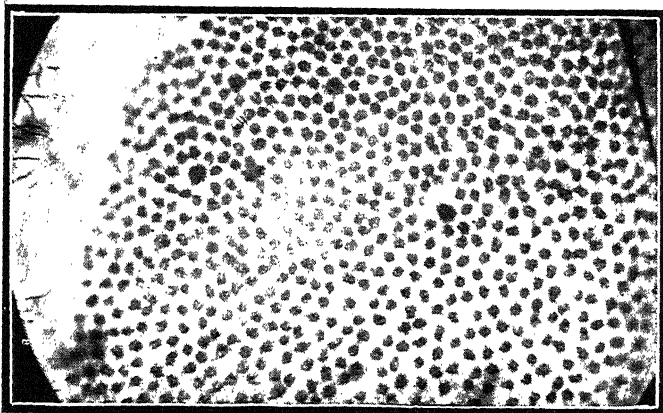


Plate III fig. 7—Photograph showing the vegetative cells in the matrix of *Volvox poonaensis*, x1,000



Plate IV, fig. 8—Photograph of ripe oospore of *Volvox poonaensis*. x1,000

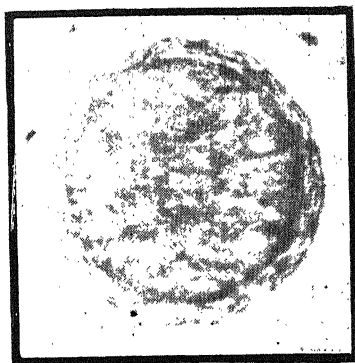


Plate IV, fig. 9—Photograph of ripe oospore of *Volvox carteri*. x1,000

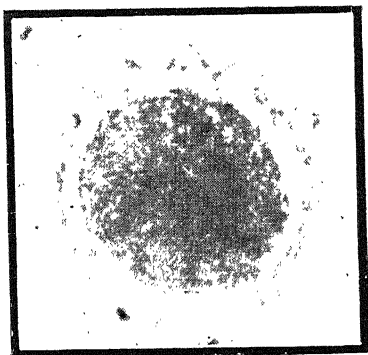


Plate IV, fig. 10—Photograph of ripe oospore of *Volvox prolificus*. x1,000

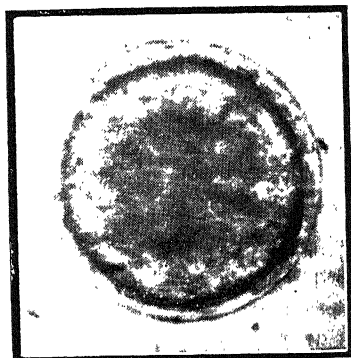


Plate IV fig. 11—Photograph of ripe oospore of *Volvox dissipatrix*. x960

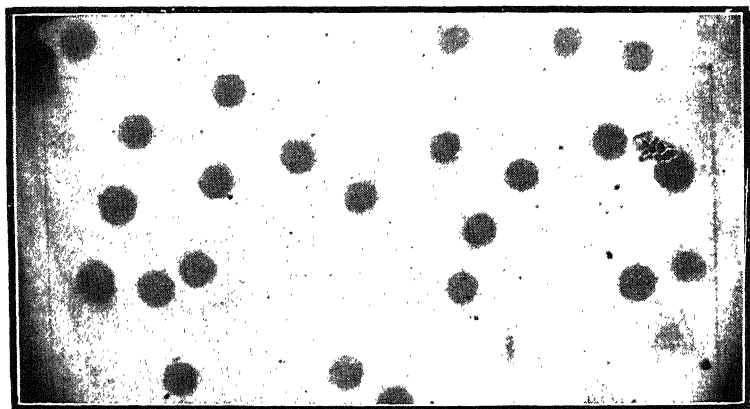


Plate IV, fig. 12—Photograph of *Volvox dissipatrix* sexual colony with oögonia and an antheridium. x120

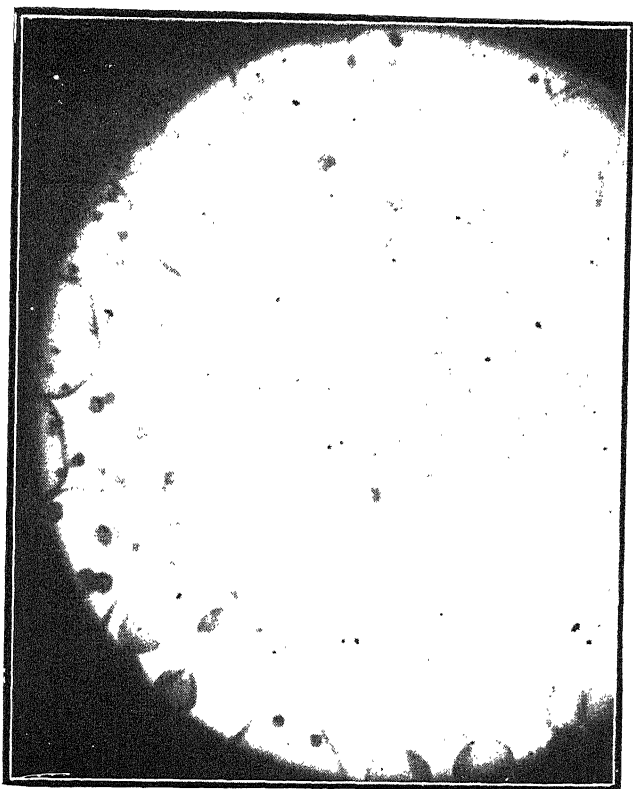


Plate V fig. 13—Photograph of *Volvox dissipatrix* with sexual and asexual colonies. x16

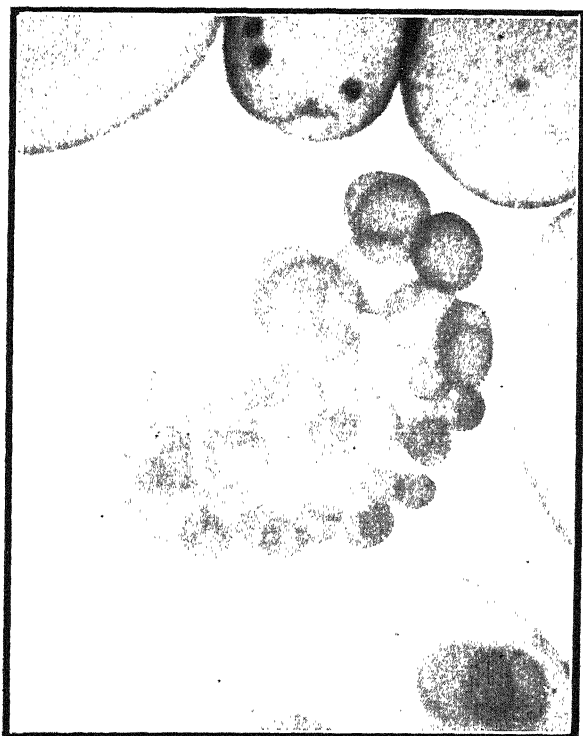


Plate V fig. 14—Photograph showing asexual colonies of *Volvox dissipatrix*. The central colony has 36 daughter colonies. x35

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A NOTE ON SOME ABNORMALITIES IN PLANTS
COLLECTED IN BOMBAY

(*With 6 Text and 5 Plate figures*)

BY

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Any deviation from the normal is always regarded with interest. In plants particularly, abnormalities have been of great use as they have shed light on some important problems. For example, the foliar nature of the stamen was recognised when the primordia of stamens were found to be transformed into petals in so-called double flowers. Abnormalities are of great value not only for solving morphological problems, but according to Gœbel we can obtain through the study of malformations a deeper insight into the homology of organs and especially of the reproductive organs in the higher plants.

The abnormalities described in this paper came our way in the course of collecting material for work in our laboratories at the Royal Institute of Science. Some of them are peculiarly interesting and these, to our knowledge, have not been reported on in India before. We have therefore described them without entering into a discussion of their causes.

(1) PROLIFERATION IN THE CAPITULA OF CALENDULA

OFFICINALIS. *N. O. Compositae*

The material (Text-fig. 1, Plate figs. 1, and 2) was collected from two flower beds in the Bhandarwada Reservoir Gardens at Mazagaon in the month of September 1933. The plants were grown from seeds ordered from England. They seemed quite healthy, most of them giving rise to normal inflorescences, with the exception of about ten or twelve plants in each bed which showed proliferation in the capitula, somewhat of the nature of that observed by Sinha¹ in *Tagetes*. As seen from the figures,

1 Sinha B. N. On a Peculiar Abnormality of Capitula in *Tagetes erecta*.
The Jour. of the Ind. Bot. Soc. Oct. 1930,

(Text fig. 1 and Plates 1 and 2) the receptacle of the primary capitulum gave rise to secondary capitula varying from ten to fifteen in number. These secondary capitula arose from the

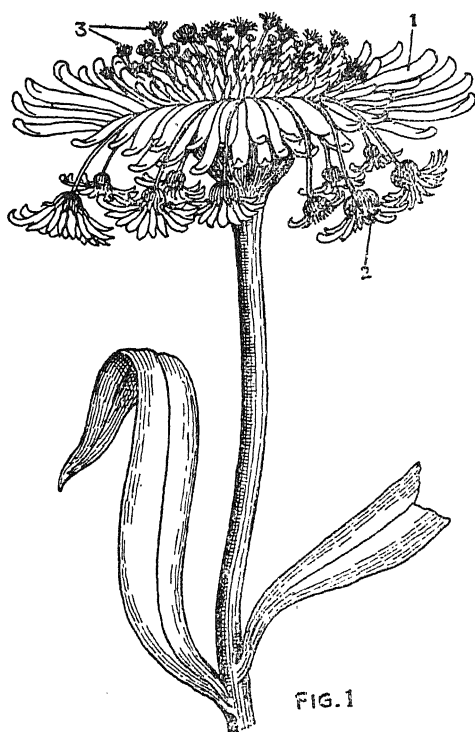


FIG. 1

Text fig. 1—Proliferation of the capitula in *Calendula officinalis*.

1...main capitulum. 2...secondary capitula from the axils of involucre bracts.

3.....secondary capitula forming a mass over the main capitulum.

axils of the involucre bracts. Their peduncles varied from 1 inch to 3 inches in length. They appeared first. A little later from all over the primary capitulum, there arose a number of secondary capitula whose peduncles did not exceed $\frac{3}{4}$ inch in length—in fact some of them were only $\frac{1}{4}$ inch in length. These also arose from the axils of bracts which were quite normal in appearance. They formed a closely-topped mass over the disc florets. Though the secondary capitula were carefully examined, no tertiary capitula were found, neither were there any petaloid or pinnatifid bracts as observed by Sinha in *Tagetes*.

Willis¹ has described the same abnormality in *Calendula officinalis* which he calls a 'hen-and-chickens' variety. But he

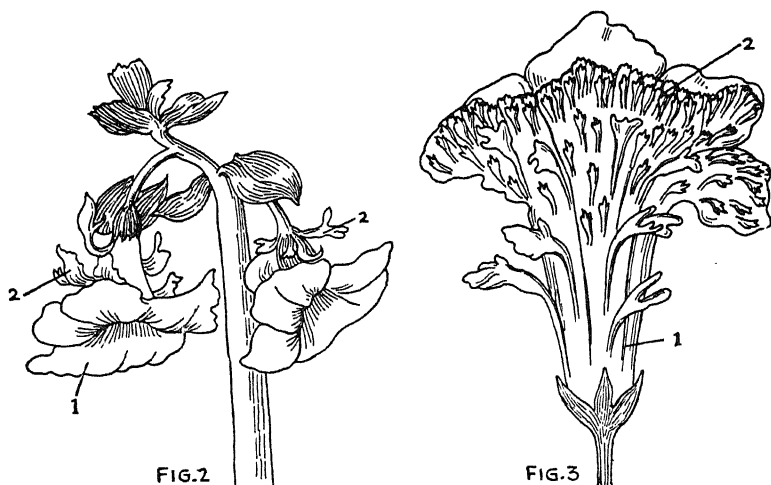
1 Willis J. C. A Manual and Dictionary of the Flowering plants and Ferns. Cambridge Univ. Press 1914.

makes no mention of secondary capitula arising from all over the primary capitulum, but only from the axils of the involucre bracts. Secondly according to Willis, the ray florets are female and the disc florets male, of both primary and secondary capitula. In this case, some of the ray florets were female and the others neuter, but the disc florets in both the primary and secondary capitula were hermaphrodite and quite like the normal disc florets. Nicholson¹ has also described a hen-and-chickens variety of *Calendula officinalis* which he names var. *prolifera* and he has also observed the same variety in the common daisy ; but he too only depicts in his diagram the secondary capitula arising from the axils of the involucre bracts.

(2) SECONDARY FLOWERS ON THE COROLLA OF PETUNIA

VIOLACEAE. *N. O. Solonaceae*

The specimens (Text figs. 2 & 3, Plate 1 fig. 3) were obtained from among a number of plants growing in a basket at the Bhandarwada Reservoir Gardens in February 1934. The plants



Text fig. 2—Rudimentary flowers on the corolla of *Petunia violacea*.
1...corolla. 2...rudimentary flower.

Text fig. 3—Rudimentary flowers on the margin of the corolla of *Petunia violacea* in large numbers.

developed flowers with the normal infundibuliform corolla, 5 stamens and the superior bicarpellary pistil. Some flowers, however, showed a peculiarity with regard to their corollas. From

1 Nicholson George, Illustrated Dictionary of Gardening, London.

the ribs of the corolla at the back, there arose about 8 to 10 small flowers about $1\frac{1}{2}$ cms. in length and $\frac{1}{2}$ and $\frac{3}{4}$ cm. in diameter at the mouth of their corolla tubes. Within these smaller flowers borne on the main corolla, there were 5 rudimentary stamens represented by thin filaments only. There was no trace of a pistil. In one case there were a few secondary flowers borne at the back of the main flower while on the margin of its corolla, there were over 20 to 30 secondary flowers forming a dense cluster. Though in cultivated forms one comes across corollas exhibiting various types of frills, lobes etc., such deviations are rare and no secondary flowers as found in this specimen have been observed.

(3) TERMINAL PHYLLODY AND PROLIFERATION OF THE FLOWERS OF *SESAMUM INDICUM*. *N. O. Pedalinae*

The plant was found in the month of November 1934 growing



Text fig. 4—Phyllody and Proliferation of the flowers of *Sesamum indicum*.

1...flower turned leaf-like. 2...leaf-like shoot arising in place of the gynaecium.

on a rubbish heap on a newly reclaimed plot of land at Colaba. It had its normal height of about 2 feet. In the lower region, it bore flowers, one in the axil of each leaf; but towards the top the branches were rather overcrowded and the flowers that appeared in the axils of the leaves here, showed not only phyllody but proliferation at the same time (Text fig. 4, Plate 1 figs. 4 and 5). These abnormal flowers were also distinguished by the absence of the gynaecium. The floral formula of the normal and abnormal flowers are given below.

Normal: K5, C(5), A4, G(2)

Abnormal: K5, C(5), A4, Go.

The calyx of the abnormal flowers consisted of five free sepals, each elliptical in outline, with acute apex and $\frac{1}{2}$ inch in length. The corolla of five petals was gamopetalous and more or less cup-shaped and digitaliform as in the normal flowers; but instead of being of the usual pinkish-white colour they were yellowish-green.

The androecium consisted of 4 free stamens while the gynaecium was totally absent. In its place, there arose a leaf-like shoot.

(4) FASCIATION OF THE PEDUNCLES OF GAILLARDIA PULCHELLA.

N. O. Compositae

The material was collected from the Institute Gardens in August 1934. The specimens showed fasciation of the peduncles of the capitula. Two or three peduncles were usually united and at the apex of the united peduncles two or three free capitula were usually borne (Text-fig 4). In a few cases however, the



FIG. 5

Text fig. 5—*Gaillardia pulchella* showing union of three peduncles but with three free capitula at the end.

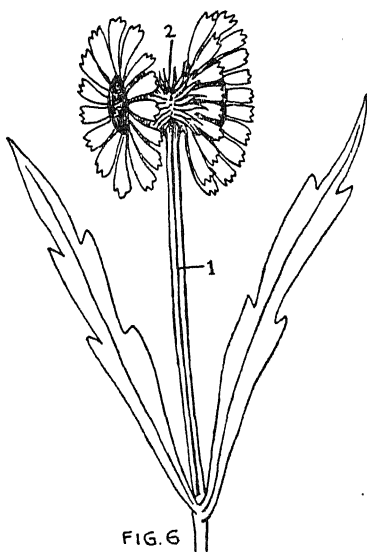


FIG. 6

Text fig. 6—Fasciation of the peduncles and receptacles of *Gaillardia pulchella*.

- 1...fasciated peduncles.
- 2.. united receptacles.

union of the receptacles of two capitula was also observed, so that it appeared as if the two capitula were joined together back to back. (Text-fig. 5). Both the disc and the ray florets were quite normal.



FIG. 1

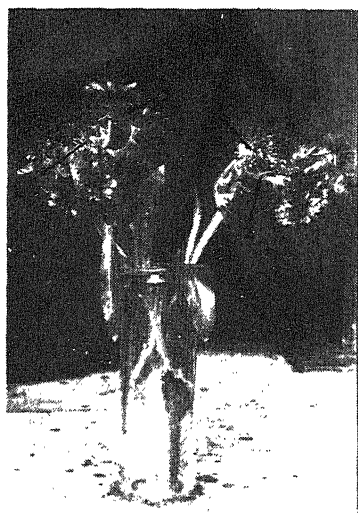


FIG. 2



FIG. 3



FIG. 4



FIG. 5

Figs. 1 and 2—Photographs showing proliferation of the capitula in *Calendula officinalis*, 1 main capitulum 2 secondary capitula.

Fig. 3—Photograph showing rudimentary flowers on the corolla of *petunia violacea*. 1 rudimentary flower, 2 rudimentary flowers on the margin of the corolla in large numbers.

Fig. 4—Photograph showing proliferation and phyllody in *sesamum indicum*. N. B.—It is difficult to distinguish the flowers which became leaf-like in photographs.

Fig. 5—A few flowers of *Sesamum indicum* which have turned green. From their centres arise leaf-like shoots, 1 Flower, 2 Leaf-like shoots,

ON THE CHROMOSOME NUMBERS IN SOME CULTIVATED AND WILD CUCURBITS OF GUJARAT

BY

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INTRODUCTION

The family Cucurbitaceae includes a very wide range of forms scattered throughout the whole of India. There are numerous cultivated plants as well as a large number of wild forms and their adequate treatment for purposes of classification forms a serious and difficult problem.

Working on the American Cucurbits, Whitaker ('33) reports that the striking variability of the external morphological characters of a number of genera and species of this family is not apparently correlated with differences in chromosome numbers. Assuming that the study of the chromosome numbers in some common Indian Cucurbits may afford some help in dealing with the phylogeny, distribution and affinities of the different species of this very interesting and economically important family, I have been investigating a number of plants during the past several months and a brief account of the results so far obtained regarding the chromosome numbers in the family is given in table I. A complete and up-to-date list of the number of chromosomes in the Cucurbitaceae is given in table II as reported by McKay ('30, '31), Whitaker ('30, '33), Gaiser ('33) and Tischler ('31).

TABLE I

| Species | Chromosome numbers | | | |
|---------------------------------------|-----------------------|-----|-----|----|
| Trichosanthes cucumerina, L | ... | ... | ... | 11 |
| Trichosanthes Anguina, L... | ... | ... | ... | 11 |
| Trichosanthes Palmata, L ... | ... | ... | ... | 11 |
| Momordica Charantia, L ... | ... | ... | ... | 11 |
| Momordica dioica, Roxb. ... | ... | ... | ... | 14 |
| Luffa acutangula, Roxb. ... | ... | ... | ... | 11 |
| Luffa acutangula var. amara, Roxb.... | ... | ... | ... | 11 |
| Luffa echinata, Roxb. ... | ... | ... | ... | 11 |
| Benincasa cerifera, Roxb. ... | ... | ... | ... | 12 |
| Coccinin indica, Wight and Arn. ... | ... | ... | ... | 12 |

TABLE II

Reported Chromosome Numbers in the Cucurbitaceae.

| Species | N | 2N | Reported by |
|---|-----|-----|-----------------------------------|
| <i>Benincasa cerifera</i> ... | ... | 40 | J. W. McKay |
| " " ... | ... | 12 | Whitaker, Sutaria |
| " <i>hispida</i> ... | ... | 24 | J. W. McKay |
| <i>Bryonia alba</i> ... | ... | 10 | Von Boenicke, Meurman |
| " <i>dioica</i> ... | ... | 10 | Strasburger, Meurman, Lindsay |
| <i>Bryonopsis laciniosa</i> ... | ... | 24 | J. W. McKay |
| <i>Citrullus vulgaris</i> ... | ... | 11 | J. W. McKay, Kozhukhow |
| " " var. <i>kleckley</i> ... | 11 | 22 | Passmore |
| " " " <i>Radio</i> ... | 11 | 22 | Whitaker |
| " " " <i>Tom Watson</i> ... | 11 | 22 | " |
| " <i>Colocynthis</i> ... | ... | ... | " |
| <i>Coccinia hirtella</i> ... | ... | 24 | McKay |
| " <i>indica</i> ... | ... | ... | R. N. Sutaria |
| <i>Cucumis Anguria</i> ... | ... | 24 | Kozhukhow |
| " <i>anguria</i> var. <i>West India</i> ... | 11 | 22 | Whitaker |
| Gherkin | | | |
| " <i>dipsaceus</i> ... | ... | 24 | Kozhukhow, McKay |
| " <i>erinaceus</i> (?)... | ... | 24 | " |
| " <i>flexuosus</i> (?)... | ... | 24 | " |
| " <i>grossularia</i> ... | ... | 24 | " |
| " <i>lyratus</i> Zim ... | ... | 24 | " |
| " <i>melo</i> ... | ... | 12 | J. W. McKay |
| " " Var. <i>Chinensis</i> ... | ... | 24 | Kozhukhow |
| " " " <i>flexuosus</i> ... | ... | 24 | " |
| " " " <i>Lake Champ-</i> | 12 | 24 | Whitaker |
| lain | | | |
| " " Var. <i>Golden Beauty</i> | 12 | ... | " |
| " " " <i>Persian</i> ... | 12 | ... | " |
| " " " <i>microcarpus</i> ... | ... | 24 | Kozhukhow |
| " " " <i>Rock Ford</i> ... | ... | 24 | Passmore |
| Cantaloupe | | | |
| " " " <i>vulgaris</i> ... | ... | 24 | Kozhukhow |
| <i>agrestis</i> | | | |
| " " Var. <i>vulgaris cultus</i> | ... | 24 | " |
| Pang | | | |
| " <i>metuliferus</i> ... | ... | 12 | 24 " McKay. |
| " <i>myriocarpus</i> ... | ... | 12 | 24 " Whitaker. |
| " <i>odoratissimus</i> (?) | ... | ... | 24 " |
| " <i>prophetarfum</i> | ... | ... | 24 " |
| " <i>sativus</i> ... | ... | 7 | 14 " McKay, Heimlich, Passmore |
| " " var. <i>Everbearing</i> ... | 7 | ... | Whitaker |
| " " " <i>Henderson</i> ... | 7 | ... | " |

| Species | N | 2N | Reported by |
|---|-----|-----|----------------------|
| <i>Cucumis sativus</i> var. Short Green | 7 | 14 | „ |
| Gherkin | | | |
| „ „ „ <i>usamtarensis</i> ... | ... | 14 | Kozhukhow |
| „ „ „ White Spine | ... | 14 | Passmore |
| Cucumber | | | |
| <i>Cucurbita digitata</i> ... | ... | 40 | McKay |
| „ <i>ficifolia</i> ... | ... | 40 | „ |
| „ <i>foetidissima</i> ... | ... | 40 | „ |
| „ <i>maxima</i> (Hubbard | 20 | 40 | Castetter |
| Squash) | | | |
| „ „ var Mammoth chili | ... | 40 | Whitaker |
| „ „ „ W a r t e d | 20 | ... | Passmore |
| (Hubbard Squash) | | | |
| „ „ | 24 | ... | Kozhukhow |
| „ „ | ... | 24 | Rau |
| „ <i>melanosperma</i> ... | 20 | ... | Whitaker |
| „ <i>moschata</i> var. Large | 24 | 48 | Castetter |
| Cheese ... | ... | | |
| „ <i>moschata calhoun</i> .. | 24 | 48 | Whitaker |
| „ „ „ | ... | 24 | Kozhukhow |
| „ <i>palmata</i> ... | 20 | 40 | McKay |
| „ <i>pepo</i> var. Eng. Vege- | 20 | ... | Passmore |
| table marrow ... | | | |
| „ <i>pepo</i> var Jessey White | 20 | ... | „ |
| Bush Squash ... | | | |
| „ „ White Luxury | 20 | 40 | Whitaker |
| „ „ var. <i>pomiformis</i> | 20 | ... | Kozhukhow |
| „ „ „ <i>citrullina</i> ... | 21 | ... | „ |
| „ „ „ Orange | 20 | ... | Whitaker |
| gourd ... | | | |
| „ „ var. Orange | 20 | ... | „ |
| gourd Long | | | |
| Island Bush | | | |
| <i>Cyclanthera explodeus</i> ... | 16 | ... | McKay |
| „ <i>pedata</i> ... | ... | 16 | 32 „ Whitaker |
| <i>Ecballium elaterium</i> ... | ... | 12 | 24 „ „ |
| <i>Echinocystis</i> (<i>Micrampelis</i>) <i>fabacia</i> | 16 | 32 | „ |
| „ „ „ <i>lobata</i> | 16 | ... | Kirkwood |
| <i>Gymnopetalum leucosticum</i> ... | ... | 22 | McKay |
| <i>Ibervillea lindeimeri</i> ... | ... | 22 | „ |
| „ sp. ... | ... | 24 | „ |
| <i>Lagenaria vulgaris</i> ... | 11 | 22 | „ Whitaker |
| „ „ | 17 | ... | Morinaga & others |
| <i>Luffa acutangula</i> ... | 13 | 26 | McKay, Sutaria |
| „ „ var. <i>amara</i> | 13 | ... | Sutaria |
| „ <i>aegyptiaca</i> ... | 13 | ... | Asana & Sutaria, |
| | | | Morinaga and others. |
| „ <i>cylindrica</i> ... | 11 | 22 | Passmore |
| „ „ | 13 | 26 | Whitaker |

| Species | N | 2N | Reported by |
|----------------------------------|----|-----|---------------------|
| <i>Luffa echinata</i> ... | 13 | ... | Sutaria |
| „ <i>gigantia</i> ... | 13 | 26 | McKay |
| „ <i>marylandica</i> ... | 13 | 26 | „ |
| <i>Melothria abyssinica</i> ... | 12 | ... | Whitaker |
| „ <i>punctata</i> ... | 12 | 24 | „ , McKay |
| <i>Memordica Balsamina</i> ... | 11 | 22 | „ , „ |
| „ <i>Charantia</i> ... | 11 | 22 | „ , „ , Sutaria |
| „ <i>dioica</i> ... | 14 | ... | Sutaria |
| <i>Sicyos angulatus</i> ... | 12 | 24 | McKay |
| <i>Trichosanthes anguina</i> ... | 11 | 22 | „ , Sutaria |
| „ <i>cucumerina</i> ... | 11 | ... | Sutaria |
| „ <i>dioica</i> ... | 11 | 22 | M. C. Das |
| „ <i>Japonica</i> ... | 11 | ... | Y. Sinoto, Sugimoto |
| „ <i>palmata</i> ... | 11 | ... | Sutaria |

MATERIAL AND METHODS

The material used in connection with this investigation consisted of seeds of cultivated varieties obtained from commercial firms. The flower buds of wild plants were collected from the hedges and fields from the vicinity of the Gujarat College, Ahmedabad.

Several fixatives, containing osmic acid, were used, but it was found that by far the best results were obtained by fixing in Karpechenko's solution as given by McKay ('31).

Solution A

| | |
|---------------------------|----------|
| Water | 65 c. c. |
| Glacial acetic acid | 10 c. c. |
| Chromic acid | 1 gram. |

Solution B

| | |
|-------------------------|----------|
| Water | 35 c. c. |
| Commercial formalin ... | 40 c. c. |

Equal quantities of solution A and B are mixed immediately before placing the material in the killing fluid. Young flower buds on removing the perianth completely, were fixed for 24 hours in the above solution, after first having been placed for a few seconds in Carnoy's fluid. As the buds sink very rapidly the exhaust pump was not used.

After fixation the material was generally dehydrated with alcohol, cleared with xylol and embedded in paraffin. Sections were cut 9 micra in thickness and stained in Heidenhain's iron-haematoxylin.

OBSERVATIONS

The chromosomes of the different species of the Cucurbitaceae here investigated do not differ considerably in outline and size; but are similar to one another in appearance. The figures were mostly drawn from the polar views of the equatorial plates of the chromosomes at the heterotypic metaphase, where they are generally well spaced and lie in a single plane. No attempt has been made to describe the details of microsporogenesis in the various species as it has already been done by Asana and Sutaria ('32) in *Luffa aegyptiaca*. The writer simply seeks to record the number of chromosomes found in some of the common Cucurbits of Gujarat.

TRICHOSANTHES

In all the species of the genus *Trichosanthes* studied in this investigation, the haploid chromosome number is 11. The chromosomes of *Trichosanthes cucumerina*, L. (Fig. 1), *T. anguina*, L. (Fig. 2), and *T. palmata*, Roxb. (Fig. 3) are almost ovoid or slightly angular in outline and more or less morphologically similar. These counts confirm the determination of *T. Japonica*, Regel. by Y. Sinoto ('29) and for *T. anguina* $2n=22$ by McKay ('31) and Whitaker ('33). Chromosome sizes differ somewhat from one species to another, but since variation in size is also found among the chromosomes in a single cell, no particular inference can be drawn from these observations. All the plants are monoecious. *T. cucumerina* is wild and commonly grows in hedges in the rains, while *T. anguina* and *T. palmata* are cultivated as vegetables. In all the species there is no unequal pair of chromosomes as described by Y. Sinoto ('29) in *T. Japonica*, which is a dioecious plant.

MOMORDICA

The haploid number of chromosomes in *Momordica Charantia*, L (Figs. 4 and 5) is 11. Both Whitaker ('33) and McKay ('31) report 11 and 22 as the haploid number of chromosomes respectively in *M. Charantia*. The individual chromosomes are more or less angular in shape and show a slight variation in size.

The haploid number of chromosomes in *M. dioica* is 14. Fig 6 represents the polar view of the heterotypic metaphase of the pollen-mother-cell, where fourteen rounded gemini of slightly differing sizes can be distinctly counted. The plant is dioecious. It is often cultivated as one of the vegetables in Gujarat, but is also found growing wild in hedges from its perennial tuberous roots during rains.

It needs to be emphasised that the number of the haploid chromosomes in the species differs from those of *M. Charantia* and

M. Balsamina, where they are only 11 as reported by McKay ('31) and Whitaker ('33). How this increase in the chromosome number has taken place is not known. It might be that this is a result of the fragmentation of some members of this chromosome complex as has been suggested for the *Salicaceae* by Blackburn and Harison ('24). Fig. 7 represents the polar view of the homœotypic metaphase, where there are 14 chromosomes of different sizes. Late anaphases of the first meiotic division which are most suitable for determining the number of the chromosomes, seem to be of short duration, and these stages are scarcely found in this investigation.

It is for the first time that the number of the chromosomes of this species has been reported and thus the genus *Memordica* affords yet another instance besides *Cucumis* and *Cucurbita* where the number of chromosomes differs in different species of the same genus.

Again it is a noteworthy feature that 14 as the haploid number of chromosomes has not yet been recorded in any plant belonging to the family *Cucurbitaceae*.

LUFFA

The genus *Luffa* is known as having 13 haploid and 26 diploid chromosomes (McKay '31, Whitaker '30 and '33, Asana and Sutaria '32, Morinaga and others '29). Working with one cultivated variety of *Luffa acutangula*, Roxb. (Fig. 8) and two wild bitter forms of *Luffa acutangula* var. *amara*, Roxb. (Fig. 9) and *Luffa echinata*, Roxb. (Fig. 10) the writer also finds the haploid chromosome number in these plants to be 13. A detailed account of the microsporogenesis in *Luffa aegyptiaca*, Mill has already been given by Asana and Sutaria ('32) and the chromosomes of the three above mentioned species of plants are also more or less angular, and both at meta and anaphase stages they do not clump together but stand well apart.

When one refers to the classification of this genus in the Hooker's-Flora of British India, one finds that there is much confusion regarding the identification of the various species. The writer agrees with McKay ('31) in saying that further work should be done in improving the nomenclature of this genus and in eliminating certain names or recognizing them as varities.

BENINCASA

The haploid number of chromosomes in *Benincasa cerifera*, Savi. is 12 (Figs. 11 and 12). It agrees with the observation of Whitaker ('33), while McKay ('31) reports $2n=40$ as the chromosome number of the same species, and 12 for *B. hispida*. It is

probable that the species *B. hispida* of McKay ('31) is really *B. cerefera* as frequently one and the same plant has been known by these two specific names. In that case *B. cerifera* of McKay ('31), containing $2n=40$ may be an entirely different species.

This plant is commonly known as the White Pumpkin or White Gourd-Melon and is largely cultivated in Gujarat for making a native sweet-meat in the cold season. The individual chromosomes are mostly angular and are the largest I have seen in the family Cucurbitaceae.

COCCINIA

The haploid number of chromosomes in *Coccinia indica*, Wight and Arn. is 12, which agrees with $2n=24$ chromosomes in *C. hirtella* as recorded by McKay ('31). The chromosomes (Figs. 13 and 14) are mostly ovoid and of fairly good size. The plant is extensively cultivated as a vegetable in Gujarat, though it also grows wild as a perennial bitter variety in the hedges throughout the year.

SUMMARY

1. The chromosome numbers of 10 Indian species of Cucurbitaceae have been determined from the pollen-mother-cell material,
2. The haploid chromosome number in *Momordica Charantia* is 11, but it is 14 in *M. dioica*.
3. The range of the haploid chromosome numbers hitherto reported for the whole family by various investigators is 7, 10, 11, 12, 16, 20, 24. To these numbers 14 is added as a new haploid number as seen in *M. dioica*.
4. A revision of the classification of the genus *Luffa* is suggested.
5. The haploid number of chromosome in *Benincasa cerifera* is 12 and not 20 as given by McKay.
6. Table II summarizes the reported chromosome numbers in the family Cucurbitaceae.

ACKNOWLEDGMENT

The work described in this paper has been facilitated by a grant received from the University of Bombay for which the writer wishes to express his sincere appreciation. Thanks are also due to Professor J. J. Asana for kindly advice and criticism.

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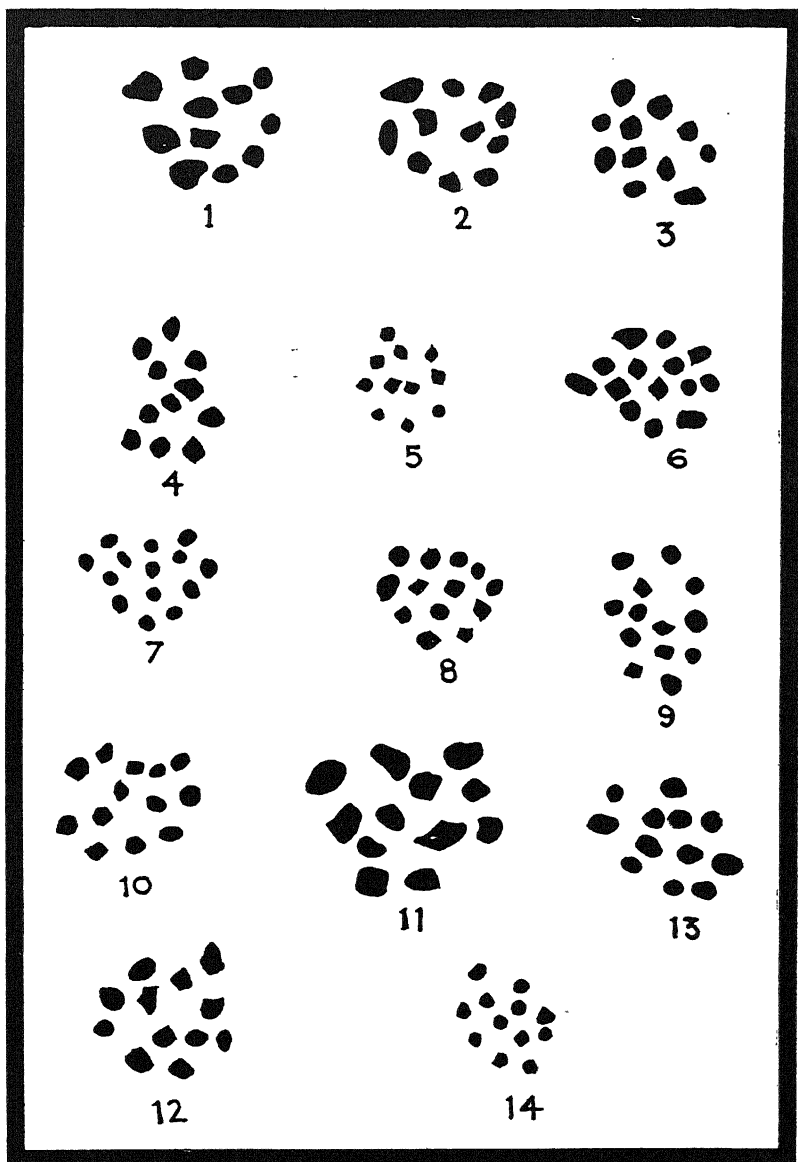
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Drawings were made with the aid of the Abbe Camera Lucida at table level. All figures were drawn under a 2 mm. immersion Zeiss apochromatic lens (N. A. 1.40) with Zeiss compensating ocular 20X. Figures reproduced without reduction.

Fig. 1 Heterotypic metaphase with 11 haploid chromosomes of *Tricosanthes cucumerina*.

Fig. 2 Heterotypic metaphase with 11 haploid chromosomes of *Tricosanthes anguina*.

Fig. 3 Heterotypic metaphase with 11 haploid chromosomes of *Tricosanthes palmata*.

Figs. 4 and 5 Heterotypic metaphase and anaphase with 11 haploid chromosomes of *Momordica charantia*.

Figs. 6 and 7 Heterotypic and homœtypic metaphase with 14 haploid chromosomes of *Momordica dioica*.

Fig. 8 Heterotypic metaphase with 13 haploid chromosomes of *Luffa acutangula*.

Fig. 9 Heterotypic metaphase with 13 haploid chromosomes of *Luffa acutangula* var. *amara*.

Fig. 10 Heterotypic metaphase with 13 haploid chromosomes of *Luffa echinata*.

Figs. 11 and 12 Heterotypic metaphase and anaphase with 12 haploid chromosomes of *Benincasa cerifera*.

Figs. 13 and 14 Heterotypic metaphase and anaphase with 12 haploid chromosomes of *Coccinia indica*.

stains were also used but Picro-Indigo-Carmine was found to be the most satisfactory. This stains the specimens beautiful blue and green, and gives them a stereoscopic appearance. For general histological study materials were fixed in either Carl's Aceto-Formol or Bouin's Fluid. The former gave better results. Sections were cut 10 microns thick and generally stained in Ehrlich's Haematoxylin, which gave complete satisfaction. Other stains, such as Delafield's Haematoxylin, Mallory's Triple, Borax Carmine, were also occasionally used.

II. HABITS AND LIFE-HISTORY

Sphaerodema rusticum Pl. I, Fig. 1 is found to inhabit shallow regions of fresh or slightly brackish water ponds which abound in vegetation. There are many such ponds in the suburbs of Bombay, and specimens were therefore available in large numbers. These ponds possess a vegetation of water-hyacinths *lemna*, and other water weeds. *Sphaerodema* is usually found clinging to the submerged parts of the water plants or to the mud at the bottom of the pond. To collect specimens, the mud from the bottom has to be dredged out and carefully searched. It is somewhat difficult to spot them in the mud as they feign death.

The insect population of the pond from which specimens of *Sphaerodema* were collected for this study, consists of two species of *Laccotrephes*—*L. elongatus* and *L. grisea*, species of *Ranatra*, *Plea*, *Notonecta*, *Microvelia*, and of aquatic beetles *Hydrophilus* and *Dytiscus*. Besides these, dragon-fly larvae and pupæ are also found. *Belostoma indica* is also suspected to live in this pond as a specimen was collected from the neighbourhood.

The different carnivorous species of fresh water fish usually found in these ponds, the water-scorpion *Laccotrephes elongatus*, and the larger beetles are to be looked upon as the natural enemies of *Sphaerodema*, since in the laboratory aquarium these predators were found to readily feed upon it. *Sphaerodema* also shows cannibalism to some extent. The ectoparasitic pupa of *Hydrachna* (Arachnida) has been found to infest *Sphaerodema*.

In the laboratory, *Sphaerodema* was observed to feed readily upon various small animals, such as—larvae and pupae of mosquitoes and dragon flies, maggots of flies, small aquatic snails, small tadpoles of frog, small fresh water fish, etc. It could also be fed on pieces of liver and flesh. The bug catches hold of the prey with its raptorial fore-legs, balances itself with the others on some support in the water, and pierces the victim with its stylets. The victim

struggles for a moment, and then lies still and in a few moments it is sucked dry.

As in some species of *Belostoma* the males of *Sphaerodema rusticum* carry the egg rafts on their backs until they are hatched. That the eggs require to be aerated on the surface of the water has been found by the fact that eggs accidentally detached from the backs of the insects and left submerged in the water fail to hatch. Detached egg rafts if placed half submerged in a flat dish hatch out in due course. The eggs placed out of water do not hatch but dry up. The method of carrying the eggs on the back of the insect is therefore a suitable means of keeping them moist in water at the same time aerating them when the insect goes to the surface to breathe.

Egg laying takes place at night and therefore it was not possible to observe it. At times a few newly laid eggs were found on the back of the male one morning, and the next morning more eggs were found added to them. That shows that sometimes it takes more than a day to complete a raft. Hoffmann (12) also has noted this fact. He states: "The eggs in a given batch are not always laid during a single deposition period, for sometimes a few eggs have been observed early in the evening and by morning many more would be present. This is also shown by the fact that hatching of a given batch often extends over two days." Hatching takes place on the ninth day after the eggs are laid. The young nymphs which emerge are pale yellow and transparent but in a few hours they become brown in colour. Mortality is very great among the young nymphs, and only a small proportion survives. Eggs are laid throughout the year, but prolific breeding takes place during and immediately after the first shower of the monsoon (July to October) when a large number of nymphs of different stages could be collected. The nymph undergoes five moults before it becomes adult. According to Hoffmann the average time taken between each instar is 7.2, 5, 5.2, 7.7, and 13.5 days respectively. The measurements of the nymphs of different stages are approximately as follows :

| Instar | I | II | III | IV | V |
|--------------|--------------|------------------|------------------|-----------------|---------------|
| Size (l x b) | 4 × 2 mm. | 5.5 × 3.5 mm. | 7.5 × 4.5 mm. | 10 × 5.5 mm. | 13 × 8 mm. |

(These are slightly larger than those given by Hoffmann.)

The adult varies in size from 15 × 8½ mm. to 19 × 11 mm. In moulting the nymphal skin splits along the mid-dorsal groove

THE MORPHOLOGY OF *SPHAERODEMA* *RUSTICUM* FABR.

BY

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and

C. J. GEORGE

Department of Biology, Wilson College, Bombay.

(With 19 Text-figures and 3 Plates)

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I. INTRODUCTION

Observations on the water-bug *Sphaerodema rusticum* of Bombay ponds kept in a small laboratory aquarium led to a study of its respiratory system which was found to possess a number of interesting adaptations for aquatic life. The results of this study are given in a separate paper (29). It was found during the course of the investigation that except for a single paper on the life-history of this insect by Hoffmann (12) there was absolutely no work done on it. A detailed morphological study was therefore undertaken. A part of this study, on the wing co-aptations, has already been published (28).

TECHNIQUE

For making chitin preparations, parts of the insect, such as the genitalia etc., were kept in a 10 per cent. solution of KOH for over twenty-four hours, washed, stained in Picro-Indigo-Carmine, dehydrated, cleared in Clove Oil, and mounted in Balsam. Other

stains were also used but Picro-Indigo-Carmine was found to be the most satisfactory. This stains the specimens beautiful blue and green, and gives them a stereoscopic appearance. For general histological study materials were fixed in either Carl's Aceto-Formol or Bouin's Fluid. The former gave better results. Sections were cut 10 microns thick and generally stained in Ehrlich's Haematoxylin, which gave complete satisfaction. Other stains, such as Delafield's Haematoxylin, Mallory's Triple, Borax Carmine, were also occasionally used.

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The adult varies in size from $15 \times 8\frac{1}{2}$ mm. to 19×11 mm. In moulting the nymphal skin splits along the mid-dorsal groove

which extends from the head to the second abdominal segment. In the head this groove bifurcates into the epicranial sutures and the cuticle of the head splits open accordingly in moulting. The newly moulted specimens are all pale yellow in colour and very soft and somewhat transparent, but a short exposure makes them dark brown as the chitin hardens and darkens.

It has been said above that *Sphaerodema* feigns death when fished out of the water. This is characteristic also of other allied insects. In feigning death the insect extends the front legs forward close to the head, and the other two pairs straight backwards and close together, and then becomes rigid. The insect remains stiff in this position for a time, but resumes activity if placed back in water. When dead, however, *Sphaerodema* does not show this posture, but has all the legs invariably stretched outwards.

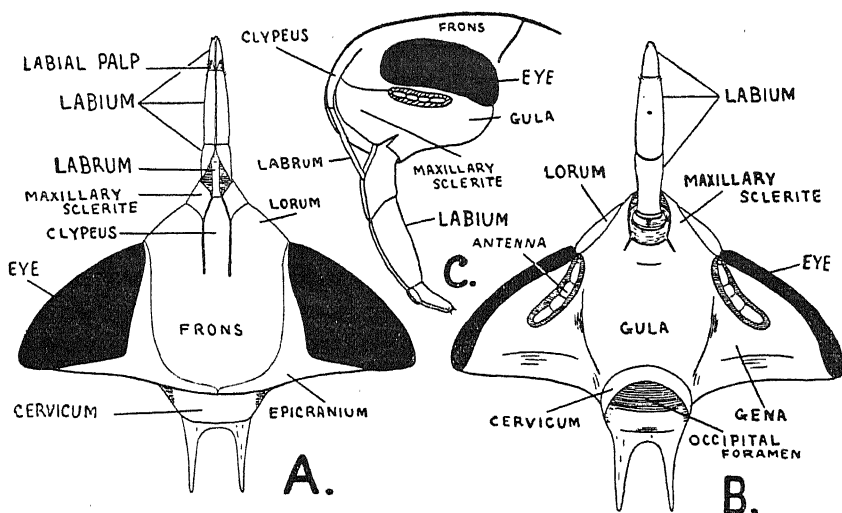
Laccotrophes and *Ranatra* behave in a similar manner, and Hamilton (11) has noted this in *Nepa cinerea*. A monograph on the subject was published by Severin and Severin in 1911 (32) from their study of this instinct in *Belostoma* and *Nepa*. Riley (30) has given a detailed account of this instinct in the water strider *Gerris*. Another noteworthy feature exhibited by *Sphaerodema*, also discussed by Riley for *Gerris*, is that of clinging to one another. Thus supported, the insects float in the water in large groups.

Sphaerodema rusticum shows two forms of adults—the normal winged and the degenerate winged. The normal winged specimens were collected in greater numbers from October 1932 to January 1933, while during the rest of that year the degenerate winged form predominated in all the collections. The next year only in one single collection made in October 1933 the full winged form appeared again in great numbers. The significance of this occasional predominance of the full winged form is not known.

III. THE HEAD

The head (Text Fig. 1.) is more or less triangular in shape, and dorsoventrally flattened. The two large triangular compound eyes are situated dorso-laterally on the head, their outer margins curving a little down to the ventral side. The anterior portions of the head curves down slightly and is prolonged into the rostrum. The small antennae are concealed in foveae on the ventral side of the head.

Dorsally the head is differentiated into its component sclerites by some indistinct sutures. Much difference of opinion exists as regards the homologies of the head sclerites in the Rhynchota as the sclerites are more or less completely fused and their sutures obliterated and it is difficult to identify the various parts with any



Text-Fig. 1—The Head. ($\times 11$) A, dorsal; B, ventral; C, lateral.

definiteness. Hamilton (11) in her paper on *Nepa* discusses at length the opinions of different investigators on this point and it is therefore not necessary to go into the details of the controversy again here. The sclerites have been named here according to the more generally accepted view on this type of insect.

THE EPICRANIUM. At the base of the head is a wide Y-shaped epicranial suture which divides the epicranium from the frons. The stem of the Y is very short and forms the median suture which divides the epicranium into right and left halves. The two arms of the Y, the lateral sutures, diverge towards the eyes and curve forwards.

THE FRONS. In front of the lateral epicranial sutures lies the frons which is a sclerite very difficult to homologue in hemipterous insects. It is a large sclerite not clearly separated from the other anterior sclerites. It was previously described as "clypeus" (Muir and Kershaw, 20) but later Muir (19) recognized it as the frons, and this view has been generally accepted now.

THE CLYPEUS. Two prominent parallel longitudinal slits with membranous connectives divide the anterior part of the head in

front of the frons into three longitudinal regions. The narrow median sclerite is the clypeus which is produced anteriorly to meet the labrum. There is no suture dividing the clypeus from the frons.

THE LORA AND THE MAXILLARY SCLERITES. The two lateral sclerites formed by the above mentioned parallel longitudinal slits are each divided by a curved suture running from each parallel slit to the anterior margin of the eye. The posterior of these sclerites are the lora on the sides of the clypeus. In *Nepa* frontal sutures divide these sclerites from the frons but in *Sphaerodema* these sutures are absent. The anterior lateral sclerites are the maxillary sclerites which curve downwards and meet the floor of the head. Between these projects the rostrum.

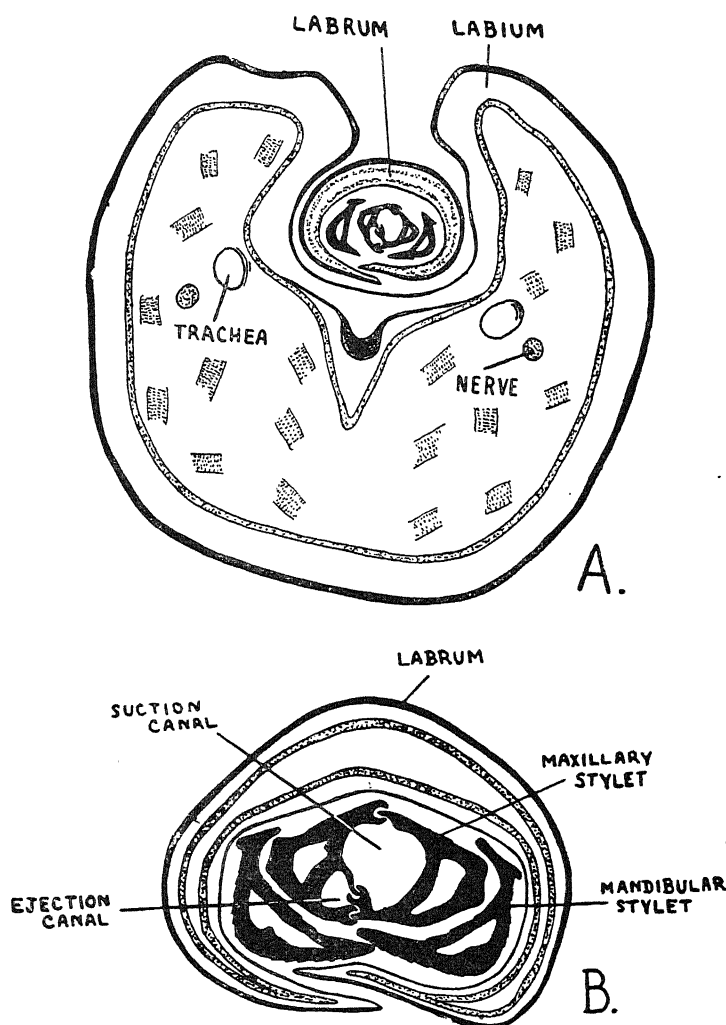
THE GULA AND THE GENA. Behind the ventral portions of the maxillary sclerites is a large sclerite, the gula. Its anterior narrow margin forms the floor of the opening through which the rostrum is projected. The sides of this opening are formed by the maxillary sclerites as mentioned above, and the roof by the labrum. The gula is broad and bulges out posteriorly. No distinct sutures separate it from the maxillary sclerites. Between the gula and the ventral, anterior margin of the eye on each side is a narrow sclerite the gena.

THE CERVICUM. Attached behind to the head is a short ringed sclerite of the neck, the posterior convex margin of which fits into the anterior median concave margin of the prothorax. From the dorsal side of the cervical sclerite project two thin apodemes inside the prothorax and to these the maxillary muscles are attached.

THE ANTENNAE. The antennae are very small and inconspicuous. They are 4-jointed. The second and third segments are prolonged laterally into outgrowths giving the antennae a branched appearance (Pl. II. Fig. 2). Except the basal segment the rest of the segments including the outgrowths bear sensory setae. The antennae are inserted on the ventral side of the head on the gena and remain in side-pockets, the foveae, below the eyes (Text Fig. 1 B). They are shorter than the head and point backwards when at rest. In this state the lateral outgrowths of the middle segments are completely hidden, only the main stems of the antennae being visible. The antennae of both the sexes are similar.

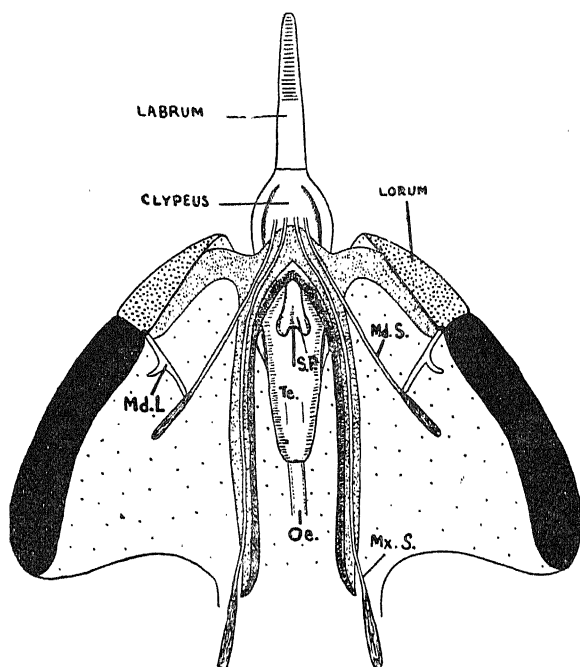
THE MOUTHPARTS. The rostrum (Text Fig. 1) is situated as usual on the ventral anterior end of the head and points backwards. The labrum can be seen leading into the dorsal groove of the labium, the basal half only being visible. For nearly three-fourths of its length from the apex it is faintly annulated. The labium is a

little longer than the labrum and considerably thicker. It is 3-jointed. The proximal joint is narrow at the base and broadens anteriorly. About the middle of its length the sides curve upwards to form the groove into which the labrum and the stylets enter. This groove is continued to the tip of the labium. The middle segment is the longest and bears at its distal end a pair of small pincer-like processes which project over the last segment on the dorsal side. These are regarded as the modified labial palps. The apical segment is the shortest and is movable. Both this segment and the labial palps bear fine sensory hairs at their tips.



Text Fig. 2—T. S. of mouth parts. A, entire rostrum $\times 200$;
B, labrum and stylets $\times 470$.

The maxillary and mandibular stylets are built on the same plan as in other aquatic bugs. They are hidden in the labial groove and the insect is seen to thrust out the maxillae occasionally at the tip of the rostrum, in the manner of a snake shooting out its tongue. The mandibular stylets are shorter than the maxillary pair, the basal attachment of the latter being far behind that of the former (Text. Figs. 3 and 4), but at the apex of the rostrum all the stylets meet in a point. Penetration is first accomplished by the mandibles which protrude out of the rostrum a little and take a grip of the tissue by means of the backwardly projecting teeth at their tips. The maxillae then follow and probe deeper into the prey than

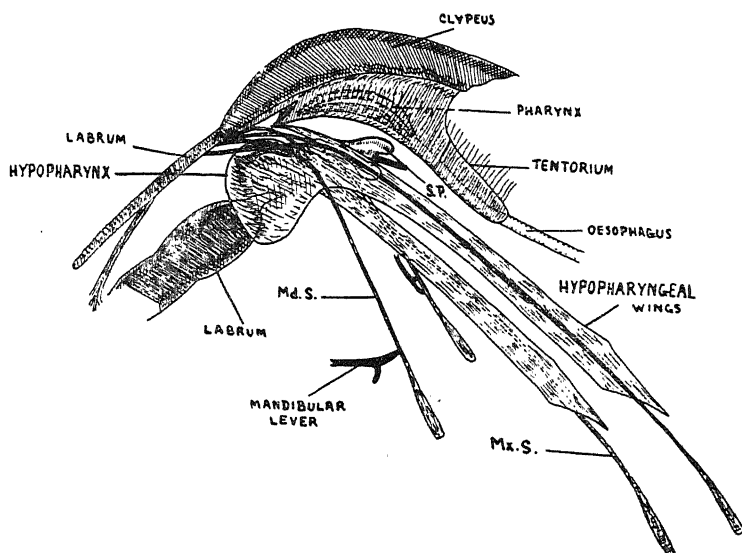


Text Fig. 3—Internal chitinous structure of the Head.
(Ventral view after removing the ventral sclerites)

the mandibles. The maxillary muscles are attached to a pair of apodemes projecting from the hind end of the head inside the prothorax. The mandibular muscle is attached to a small lever placed below the posterior end of the genal suture. The Mandibular stylets bear on the outer margins of their tips six or seven sharp backwardly pointed teeth which as mentioned above help to take a firm hold of the prey. The inner sides of these stylets are grooved and when apposed form a tube into which the

maxillary stylets lie. The maxillary stylets bear their apices a number of fine denticles. The two maxillary stylets are interlocked and move as one. Their inner sides bear double grooves forming two channels, the dorsal for suction and the ventral for saliva injection. When the insect is observed feeding, the movement of the liquid in the suction canal can be easily made out. The ejection cannal does not lie exactly below the suction canal but is placed slightly to the right as can be seen from transverse section (Text Fig. 2 A and B). This is because the lower groove of the right stylet is deeper than that of the left.

THE INTERNAL CHITINOUS STRUCTURE OF THE HEAD. Arising from the sides of the clypeus and projecting down into the head, is a boat-shaped chitinous structure which supports the pharynx (Text. Figs. 3 & 4. Te.). Muir (19) in *Cicada* and Hamilton



Text Fig. 4—Internal chitinous structure of the Head dissected out.
(Lateral view).

(11) in *Nepa* regarded this as the fused anterior arms of the tentorium. The oesophagus which enters the head through the small opening between the brain and the sub-oesophageal ganglion ends in a chitinous structure, the pharynx, which runs dorsal to the tentorium. The pharynx is W-shaped in transverse section (Pl. II Fig. 14) the median ridge of which bears a row of fine long hair. The pharyngeal muscles are attached to the clypeus above and the

pharynx acts as a suction pump. The pharynx and the oesophagus can be easily separated from the fused arms of the tentorium in *Sphaerodema* as was noted by Muir (19) in *Cicada*. Hamilton (11) states that in *Nepa* the floor of the pharynx "appears to be connected with the fused anterior arms of the tentorium".

The base of the labium is connected with a semi-chitinous rounded capsule which is produced posteriorly into two strap-shaped arms upto the neck region. The dorsal wall of this capsule is notched and the stylets pass over this into the rostrum. This is regarded by Hamilton as the hypopharynx and the two arms as "hypopharyngeal wings", differing from Awati (1) who regarded the hypopharynx as the body of the tentorium and the two arms as the posterior arms of the tentorium. Laterally the hypopharynx is connected to the maxillary plates. The "hypopharyngeal wings" are grooved on the outer sides and the maxillary stylets run along these (Figs. 3 and 4). These arms therefore serve as guides to the maxillary stylets.

Below the tentorium lies the salivary pump (Text. Figs. 3 and 4) which is prolonged anteriorly into the ejection canal of the maxillae.

IV. THE THORAX

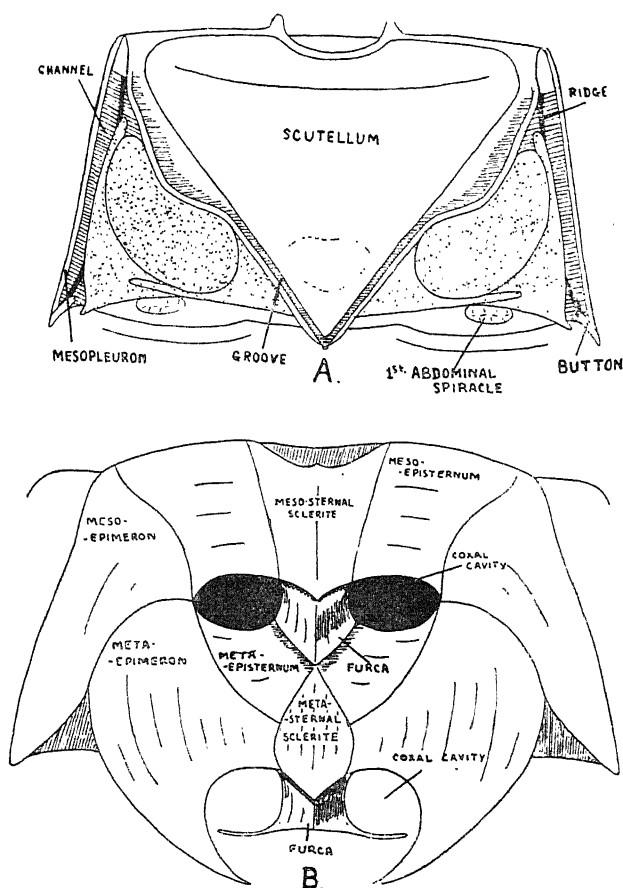
In the entire animal the prothorax and the scutellum alone can be seen on the dorsal side, but when the wings are removed the sides of the metathorax are exposed to view, the middle portion of the latter being hidden under the scutellum. The head and the thorax measure about half the total length of the insect.

THE PROTHORAX. The prothorax (Pl. I. Fig. 1.) when taken with the triangular head forms another larger triangle. The anterior margin of the pronotum is slightly concave in the middle region and into this fits the cervical sclerite. The posterior margin is unbroken and is fringed with short fine hair. A prominent suture runs along the four sides of the pronotum leaving a narrow border on the anterior side and a broad border on the other three sides. A median longitudinal suture runs from the anterior to the posterior suture. The lateral borders of the pronotum are paler in colour than the rest of the surface, and match with the lighter coloured embolia of the hemelytra which follow them. The whole of the posterior border marked off by the suture overlaps the anterior part of the mesonotum which is smoothly curved down to facilitate the movement of the prothorax on it. The hair on the posterior margin prevents water from entering the prothorax.

In the nymphs the marginal suture of the pronotum is not so prominent and leaves only a narrow border all round. The median longitudinal suture seems to be in continuation with the median epicranial suture anteriorly, and is also continued backwards into the meso- and meta-nota and the much reduced first two abdominal segments. In moulting the nymphal skin splits along this longitudinal suture from the head to the second abdominal segment.

The prosternum in both the nymph (Text Fig. 9) and the adult, is smaller than the pronotum and is divided into a median sternal sclerite with a median longitudinal ridge and two triangular pleurites. The coxal cavities are placed on the outer margin of the anterior region of the prosternal sclerite.

THE MESOTHORAX. The mesonotum (Text Fig. 5A) consists only of the scutellum which overlaps the metanotum. The two



Text Fig. 5—Meso- and Meta-thorax. ($\times 11$) A, meso- and meta-nota;
B, meso- and meta-sterna.

lateral margins of the scutellum are deeply grooved and into these the inner margins of the hemelytra fit.

The mesosternum (Text Fig. 5B) is large and bears near its posterior margin the coxal cavities with the furca placed between them. The pleura are distinctly divided into the episterna and the epimera, the latter extending backwards upto the abdomen. The outer margins of the epimera curve over to the dorsal side a little, thus enclosing a channel on either side of the metathorax (Text Fig. 5A). The spiracles of the metathorax open into these channels. A longitudinal ridge divides each channel into two. The posterior end of this ridge bears a button which fits into a corresponding socket on the hemelytron, and thus fastens the hemelytron to the side of the body.

In the nymphs the mesonotum is distinct; the posterior margin of it is somewhat sinuate, and forms three backward projections. The sinuation is very slight in the early stages of nymphs but becomes deeper in the later stages, and from the two lateral projections the wing pads grow. The nymphal epimera (Text Fig. 13) are flap-like and free distally, and hold a small quantity of air around the metathoracic spiracles which they cover.

THE METATHORAX. The metathorax is firmly articulated with the mesothorax. The middle portion of the metanotum (Text Fig. 5A) is covered over by the scutellum.

The metasternum (Text Fig. 5B) is situated between the backwardly projecting epimera of the preceding segment and projects over the first two abdominal sterna. The metasternal sclerite is small and shield-shaped; the pleura are divided into small episterna and large convex epimera. The coxal cavities are placed on the posterior margin.

In the nymphs the metanotum is distinct during the earlier stages but is gradually more and more pushed under the mesonotum as the nymph advances, till in the fifth instar only a bit of it is visible. The meta-epimera bear semicircular out-growths (Text Fig. 9) which extend over the abdominal sterna and serve to hold a quantity of air around the abdominal spiracles.

THE WINGS. We have already described in a separate paper (28) the dimorphism and the various locking arrangements of the wings of *Sphaerodema rusticum*.

The Hemelytra.—In the normal winged form the hemelytron (Pl. I. Fig. 1) bears a well developed membrane which is scantily veined. The venation is not uniform but shows individual variation. This membrane is entirely missing in the degenerate

winged form. The basal coriaceous portion of the hemelytron has very indistinct venation. A well marked embolium is present which is lighter in colour than the rest of the coriaceous portion.

The Membrane Wings.—The second pair of wings in the normal form Pl. I. Fig. 1 is of the usual type being thin, membranous and triangular in shape. It is a little shorter than the hemelytron but very much broader, and is therefore folded along the anal region. The costal margin is slightly turned upwards in some part and is in that part dented.

The homology of the veins in this group of insects is a matter of some controversy. As commonly recognized the costal vein is merged with the subcostal and is not distinguished in the imaginal wing. The subcostal, radial and median veins unite at their apices to form two longitudinal cells. They give out a number of transverse branches but these are not so well developed and the wing remains delicate. The cubital is unbranched and is convex distally. In the anal region two short anal veins are present.

THE LEGS. The three pairs of legs are somewhat dissimilar being modified to perform different functions, though on the bottom of the pond all the three pairs are used for ambulatory purposes.

The Prothoracic Legs.—The fore-legs are raptorial, being short and stout and perfectly modified for the function of seizing and holding the prey. They are also used for grasping water plants for support. They start very close together from the anterior region of the prothorax and when the bug is at rest on the surface of the water they are folded so close to the restum that they are not visible from the dorsal side. The coxa is long and bears a shallow depression on the upper side for the femur to rest when folded. The trochanter is small and articulated to the base of the femur and movable along with it on the coxa. The femur is very broad and flat and a little longer than the coxa. It bears a few stout spines on the upper surface. The lower edge is grooved and into this the tibia and tarsus fit, like the blade of a pen-knife fitting into the handle, when folded. Along the groove are short fine hair. The tibia is narrow and a little shorter than the femur, and together with the tarsus can be completely folded on the femur. All along its lower edge are present short fine hair. The tarsus is very short and single-jointed both in the nymph and the adult, and bears a pair of small claws. The lower surface of the tarsus also bears short fine hair.

The Mesothoracic Legs.—The middle legs are longer than the front ones. The coxa and trochanter are more or less similar to those of the front legs but the femur is narrow and elongated. The

femur bears a slight groove on its lower margin for the reception of the tibia but it does not make a perfect fit as in the fore-legs. The tibia is about as long as the femur and bears numerous stout spines. Both the upper and the lower margins of the tibia are fringed with long fine hair. At its distal end the tibia bears a short blunt spur bearing a cluster of spines. The tarsus is three-jointed in the adult but only single jointed in the nymph and bears a pair of claws. These legs are purely ambulatory.

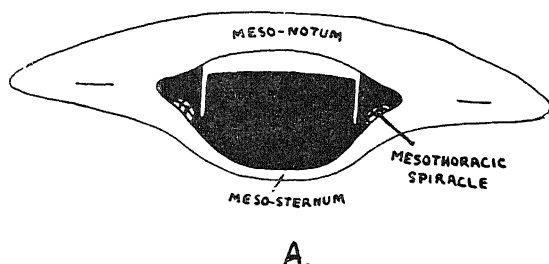
The Metathoracic Legs.—The hind legs are the longest, and all the segments are generally like those of the middle legs. Distally the lower margin of the femur bears long fine hair which is continued all along the margin of the tibia and tarsus and it serves the insect in swimming, as the insect uses its hind-legs as a pair of oars in the water. In *Belostoma* the hind tibia is flattened for the same purpose. The distal end of the tibia bears a spur like the one on the mesothoracic tibia but longer and provided with a thick cluster of spines. The insect is often seen to brush the tip of its abdomen with its hind-legs in order to remove the air bubbles coming out of the sub-elytral space, and the spiny spurs aid in the process. In the nymph the spurs are used to break the film of air carried on the ventral side of the abdomen when necessary. The tarsus is three-jointed in the adult but only one-jointed in the nymph; it bears two prominent claws.

Belostoma differs from *Sphaerodema* in having the fore-tarsus of the adult two-jointed with only a single long claw. *Laccotrephes elongatus*, *L. grisea*, *Nepa cinerea* and *Ranatra sp.* all have single-jointed tarsi in all the three pairs of legs, but the fore-tarsi bear single claws. Both *Belostoma* and *Sphaerodema* possess three-jointed tarsi on the second and the third pairs of legs. Distant (9) wrongly describes them as two-jointed, the first small segment being apparently overlooked by him.

THE NYMPHAL AIR-FLAPS. In the nymph all the spiracles including those on the thorax are situated on the ventral side. Hence some means is necessary by which the young insect could take the atmospheric air to these spiracles. The ventral side of the thorax of the nymph therefore has developed chitinous "air-flaps" for enclosing air (Text Fig. 9). These are semicircular transparent outgrowths from the meta-epimera, which extend over a great part of the abdomen, reaching to the middle of the fifth abdominal segment. On their distal margins they bear long fine hair and short stout spines. The flaps and the membranes of long hair which project from them enable the insect to imprison a small quantity of air between them and the body. The anterior margins of the

air-flaps lie in apposition to the projecting posterior margins of the flap-like mesosternal epimera, and hence the space enclosed between the former and the abdomen and metathorax is continuous with that between the ventral side of the mesothorax and the latter. In this manner all the ventral spiracles of the nymph open into an air chamber and are thus prevented from being wetted. When the nymphs of *Sphaerodema* are seen swimming about in the water the posterior aspect of the air-store appears as a glistening bead on the ventral side of the abdomen. The purpose of this air is the same as that of the air under the hemelytra of the adult, viz. respiratory.

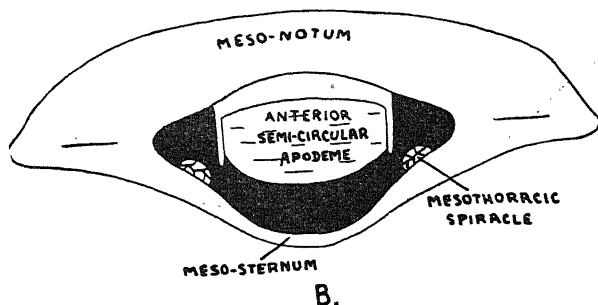
Martin (17) was the first to record these metasternal flaps in the Belostomatidæ. He suggested that besides their preventing the



Text Fig. 6—Anterior view of mesothorax showing endo Tergite. ($\times 15$).

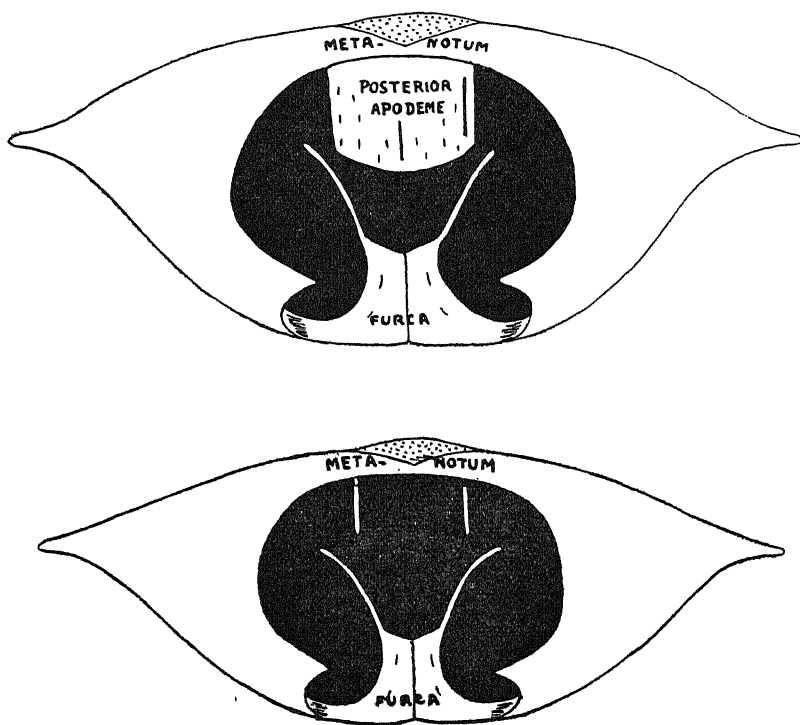
A, degenerate form ; B, normal form.

abdomen from being wetted, they might have a respiratory function like the tracheal gills of the larvae of *Agrion*. But this view cannot be accepted as the tracheal supply of these organs is nothing compared to that of a tracheal gill. That they serve only for enclosing air under the abdomen for the purpose of protecting the spiracles from water and that this stored up air is used by the insect for respiration—is experimentally proved and described in another paper (29).



THE ENDOSKELETON OF THE THORAX. Inside the meso- and meta-thorax are found several chitinous pieces which form the endo-skeleton of the thorax. They are developed from the terga, the sterna and the pleura, and are described below under these heads.

The Endotergites.—The anterior margin of the meso-notum is curved down and on the sides meets the slightly turned up anterior margin of the meso-sternum (Text Fig. 6A). In the middle a small opening is left for the internal organs to pass through. In the normal winged form the aperture is further reduced by the development from its dorsal margin of a semi-circular apodeme (Text Fig. 6 B) which projects vertically downwards in the mesothorax. To this phragma the anterior ends of the dorso-longitudinal muscles (tracheo-parenchymatous organs) are attached. From the posterior margin of the metanotum, which lies a little anterior to and below the apex of the scutellum, hangs downwards a broad curved apodeme (Text Fig. 7 B). To this the posterior



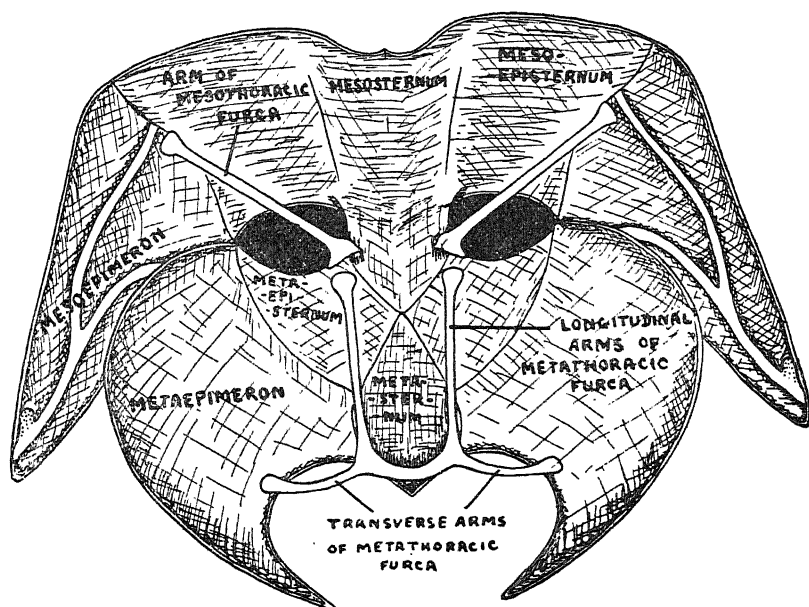
B

Text Fig. 7—Posterior view of meta thorax showing endosternite and furca. (× 15) A, degenerate form ; B, normal form.

ends of these muscles are attached. From the sides of this posterior apodeme arises a pair of thin apodemes which projects vertically downwards and has their free ends knobbed for the attachment of the posterior ends of the oblique lateral muscles of the mesothorax. Anteriorly these muscles are attached to the ventrally curved anterior margin of the mesonotum. The posterior apodeme and the pair of thin apodemes appear to arise from the posterior portion of the scutellum with which the metanotum is completely fused.

In the degenerate winged form where the tracheo-parenchymatous organs are absent, the anterior semi-circular phragma and the posterior phragma are wanting. In place of the anterior phragma a pair of rod-like apodemes (Text Fig. 6 A) is found indicating the limits of the semi-circular apodeme of the normal form. The pair of thin metathoracic apodemes is however present (Text Fig. 7 A) as in the normal form, though the muscles are wanting.

The Endosternites.—Immediately below the posterior endotergites lies the furca of the mesosternum, which consists of a small basal piece which remains outside the body, and a pair of thin arms projecting towards the meso-epimera (Text Figs. 7 & 8).



Text Fig. 8.—Dorsal view of Meso- and Meta-Sterna showing endosternites. ($\times 15$)

The posterior portion of the metasternum bears a well developed furca which possesses two pairs of slender arms; one, a pair of transverse arms forming the upper margins of the coxal cavities, and the other, a pair of parallel longitudinal arms extending upto the mesothoracic furca. The latter affords protection to the mesothoracic ganglionic mass.

The Endopleurites.—The endopleurites consists of two small “jugular sclerites” attached to the pronotum. They give attachment to the prothoracic leg muscles.

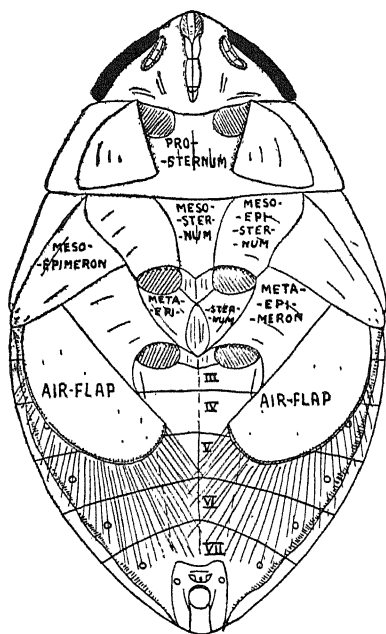
V. THE ABDOMEN

The abdomen of adult *Sphaerodema* is very much concave on the dorsal side and forms a cavity for the storage of air for respiration. In the nymph both the terga and the sterna of the abdomen are convex. The lateral margins of the abdomen in both the nymph and the adult bear short, stout spines and a row of fine hair which help to balance the insect in water.

THE TERGA. The first seven segments of the abdomen only are

visible eternally in the adult. Their terga are thin and transparent and are covered with long hairs which are hooked at the tips. The first segment which is narrower than the second overlaps the latter to a certain extent. The seventh tergum is made up of a median bi-fid and two side pieces.

In the nymph the first nine terga can be distinguished, and the first as in the adult overlaps the second. The eighth is a small horse-shoe shaped tergite and in between the arms of this lies the ninth tergum. The terga are not thin and hairy as in the adult.

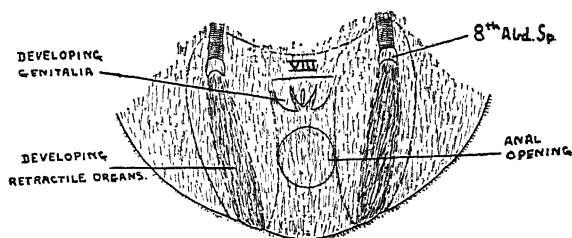


Text Fig. 9—Ventral view of Nymph.

THE STERNA. The sterna of the adult are thick unlike the terga and more chitinated. Six segments, from 2nd to 7th, are

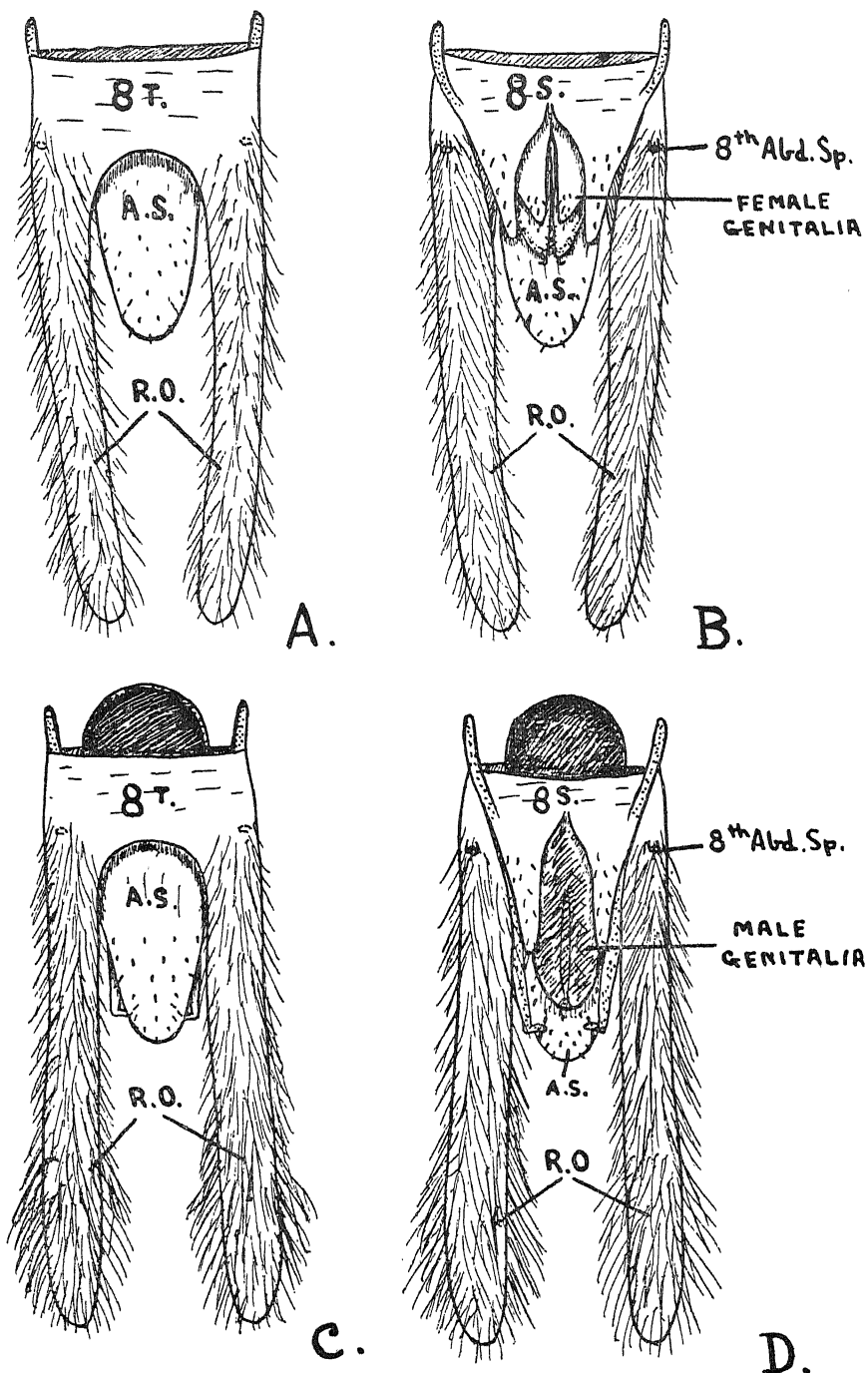
only visible. The first which is present as a membranous piece is entirely hidden by the projecting metasternum. The second sternite is also very much reduced and is visible only as two small triangular marginal pieces. The fifth and the sixth sterna are more or less completely fused, the dividing suture being not distinguishable except towards the margin. The seventh sternum is made up of three pieces like the seventh tergum ; but the middle piece is entire with a rounded posterior margin. A median longitudinal suture divides the sterna 3 to 6 each into two pieces. A longitudinal marginal suture divides each half into two unequal parts. The two marginal sutures extend from the second to the sixth sterna, and meet the inner margins of the lateral pieces of the seventh sternum.

In the nymph sternites two to eight can be made out (Text Fig. 9). Behind the eighth the segmentation is not clear but a large round anal piece represents the tenth segment, while in the fourth and the fifth instars the developing gonapophyses (Text Fig. 10) can be distinguished anterior to the anal piece and this region therefore represents the ninth segment. The nymphal sterna are thin and covered with long hooked hair all over the surface.



Text Fig. 10—Hind view of the abdomen of the Nymph in the fifth stage (Ventral view showing developing genitalia and retractile organs).

THE RETRACTILE ORGANS. Two strap-shaped organs (Text Fig. 11. R. O.) which can be retracted into the hind region of the abdomen are characteristic of the family Belostomatidae. The straps bear long hydrofuge hair directed backwards. Ventrally at the base of each of these opens the last (eighth) abdominal spiracle. From observations on nymphal development we conclude that the major portion of the eighth segment is utilized in the formation of the retractile organs. In the nymph the eighth segment, as described above, is horse-shoe shaped, and the arms of this horse-shoe reach the tip of the abdomen (Text Fig. 9). Between these arms develop the genital and anal segments. The future

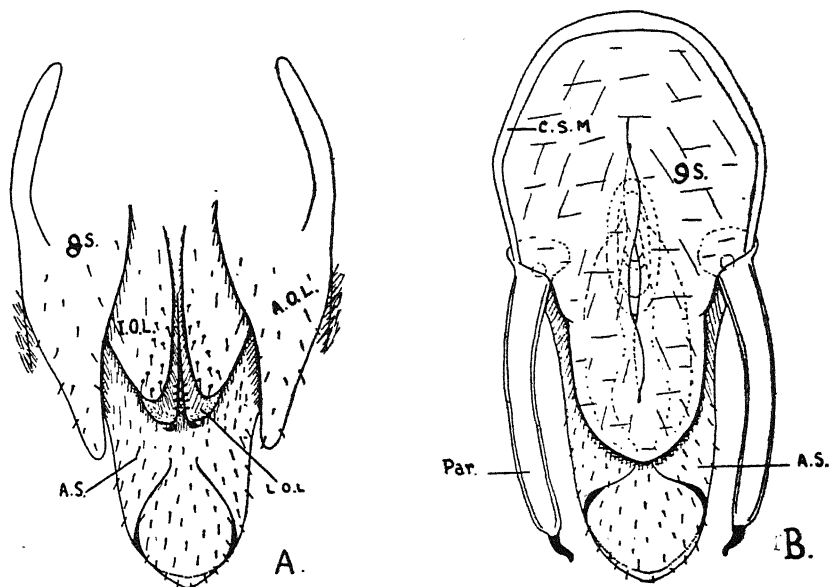


Text Fig. 11 —Retractable Apparatus (including the Retractable Organs, Genitalia and Anal Segment). $\times 22$ A, Female (dorsal view); B, Female (ventral view) C, Male (dorsal view); D, Male ventral view).

retractile organs grow inside these arms and at the last moult they come out in their typical form. The retractile organs are therefore not appendages of the eighth segment but the drawn out lateral parts of the eighth segment itself. Anteriorly the tergum of this segment is represented only by a membranous piece connecting the two straps, while the sternum consists of two triangular pieces which support the genitalia. Bueno (3) described the origin of these "retractile strap-like appendages" in the Belostomatidae as: "the lengthened peritreme of the sixth abdominal spiracles". By "sixth" of course he meant the last pair of spiracles.) For the Nepidae he says: "the two halves (of the siphon) are nothing but the lengthened peritreme of the seventh pair of abdominal spiracles". Hamilton described the siphon of *Nepa* as the prolonged paratergites of the eighth segment. Our observations are therefore not in agreement with those of the above authors.

THE ANAL SEGMENT AND THE GENITALIA. Between the two retractile organs are seen the genitalia, covered dorsally by the anal segment (Text Fig. 11). The anal segment is a narrow elongated cylindrical structure at the termination of which opens the anus. The distal half of the segment is covered with short fine hair.

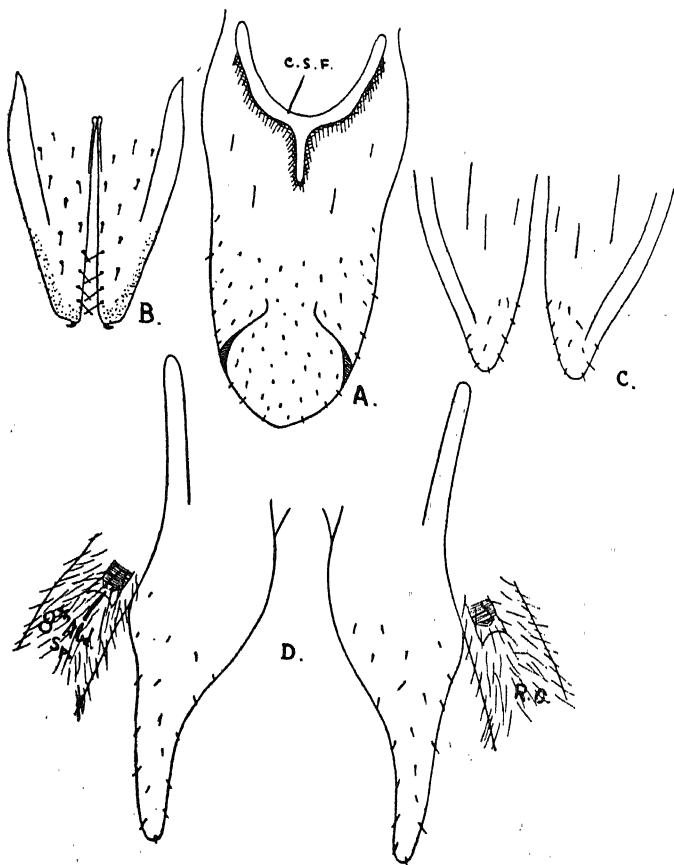
The Female Genitalia.—The ovipositor is insipient and consists only of two pairs of short triangular plates protected ventrally by the two triangular anterior sternites of the modified eighth segment (Text Figs. 11 B and 12 A). The plates are on the whole



Text Fig. 12—Genitalia (ventral view). $\times 33$. A, female, B, male.

feebly chitinized, the well chitinized region being limited to the outer borders. Between the ovipositor and the anal segment is a forked chitinous piece (C. S. F. Text Fig. 13 A) which affords attachment to the genital plates on its ventral side and to the anal segment on its dorsal side. The dorsal plates, the lateral ovipositor lobes, are longer than the ventral plates, the inner ovipositor lobes. Each lateral ovipositor lobe bears at the tip a small outwardly curving chitinous hook. The inner margins of these lobes bear interlocking hair. The inner ovipositor lobes are broader and more membranous than the lateral. There are no anterior ovipositor lobes, unless the two anterior sternal pieces of the eighth segment are regarded as representing them.

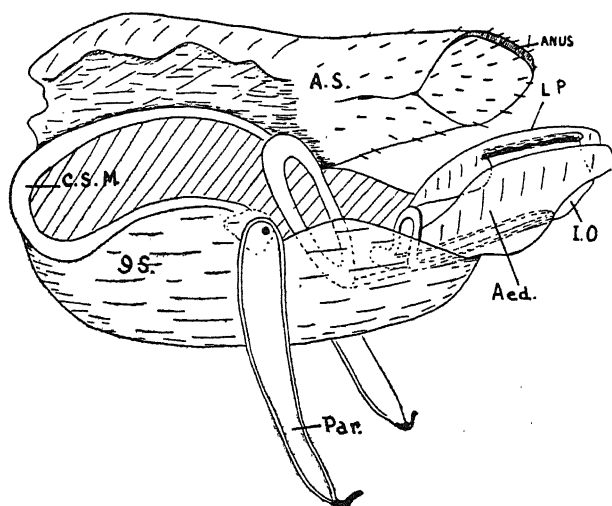
The Male Genitalia.—The male genitalia are formed by the ninth segment (Text Figs. 11 C and D, 12 B, and 14). The



Text Fig. 13—Parts of Female Reproductive Organs. $\times 33$. A, Anal segment
B, Lateral ovipositor lobes ; C, Inner ovipositor lobes ;
D. Anterior ovipositor Lobes.

sternum of the ninth segment forms a hollow boat-like structure. This is found to be made up of a pair of plates. Anteriorly this structure is attached to the base of the anal segment by a curved chitinous rim, which corresponds to the forked chitinous support of the female. The parameres are hinged on the outer side of the boat-like structure to the ends of this chitinous rim. Inside the boat-like structure lies the aedeagus.

The aedeagus (Text Fig. 14, Aed.) consists of two lateral leaf-like plates (L.P.) and a median short stout intromittent organ (I.O.) The entire structure is supported ventrally by a chitinous rod which at the anterior end is continued into a large stout chitinous ring at

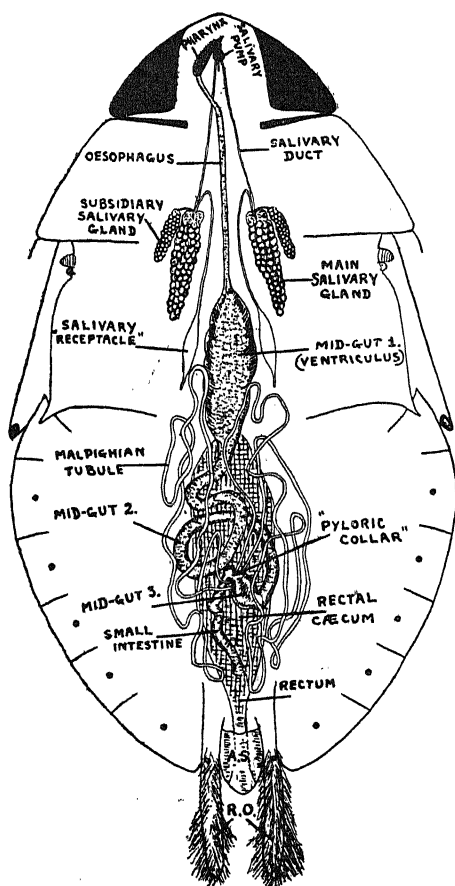


Text Fig. 14—Parts of Male Reproductive Organs. (Lateral view of Anal Segment and Genitalia). $\times 33$.

right angles to the rod. The protractor muscles of the aedeagus are attached to the dorsal part of this ring. Posteriorly the ventral chitinous rod bifurcates. The two arms bend dorsally upon themselves and form the ventral supports of the lateral leaf-like plates of the aedeagus. These arms are then continued forwards and they converge into a smaller vertical ring lying just behind the larger one. This smaller ring forms the base of the intromittent organ. The two rings and the chitinous rods are connected with one another by membranes. The stout intromittent organ is knobbed at the tip and the gonopore opens on its dorsal side by a slit. The lip bounding this opening is thickly covered with short fine hair.

V. THE DIGESTIVE SYSTEM

THE FORE-GUT. The fore-gut (Text Fig. 15) extends into the mesothorax and consists of the pharynx and the oesophagus. The suction canal of the maxillary stylets leads into the chitinous pharynx which lies immediately below the clypeus. It is supported ventrally by a strong chitinous trough, the so-called fused anterior arms of the tentorium, suspended from the sides of the clypeus. The dorsal wall of the pharynx bears on the outside a median longitudinal row of fine long setae. In transverse section the dorsal wall is W-shaped (Pl. II. Fig. 14) and between this and the clypeus lie the pharyngeal muscles.



Text Fig. 15—The Digestive System.

The oesophagus is very long and narrow and is somewhat elastic. The epithelial lining of the oesophagus is made up of elongated cells with a chitinous intima (Pl. II. Fig. 13). The muscular wall is made up of an inner circular and outer longitudinal layers of muscles.

THE MID-GUT. The mid-gut is divided into three distinct regions, a large sac-like anterior ventriculus, a coiled tubular middle portion, and a small posterior rounded chamber. In a transparent living specimen of the insect the ventriculus may be occasionally seen to contract peristaltically. The epithelial lining of this part of the alimentary canal shows groups of columnar secreting cells (Pl. II. Fig. 15). At the base of each group are a few small cells clustered together. These are the regenerative or "nest" cells (Pl. II. Fig. 15, N.C.). An inner layer of circular and an outer layer of longitudinal muscle fibres lie on the outside. A basement membrane lies outside the epithelial layer, and a peritonal membrane covers the muscular layer.

The middle region of the mid-gut, the narrow coiled tube lying in the abdominal region, has a structure similar to that of the preceding one.

In the terminal portion of the mid-gut, the swollen rounded chamber, are frequently found collected small fine particles of a dark brown colour. A narrow "pyloric collar", connects the mid-gut to the hind-gut, and into this region opens a pair of Malpighian tubules.

THE HIND-GUT. The mid-gut opens into the hind-gut laterally at its anterior end. The anterior region of the hind-gut is distinguished as the small intestine. It is a straight short tube which opens behind into a thin-walled rectal caecum. The epithelial lining of the small intestine is very peculiar and resembles somewhat the lining of the large intestine of mammals (Pl. III. Fig. 16). The entire epithelium with its basement membrane is thrown into convolutions. The epithelial cells are elongated and bear large oval nuclei, and their cytoplasm is striated. The muscular lining of the wall is very thin. Only a few thin longitudinal fibres can be made out. The epithelial tissue is penetrated by a few fine tracheoles (Pl. III. Fig. 16). Poisson (26) had noted such intracellular tracheae in *Nepa*. Hamilton (11) disagreed with him and maintained that they were only "small round holes". It is a misapprehension on the part of Hamilton, because Poisson noted these small holes in addition to the intracellular tracheae: "Entre ces trachées s'observent de nombreuses vacuoles". His figure xvi

also indicates both the tracheae and the vacuoles. Oblique sections clearly reveal tracheoles penetrating the epithelial tissue (Pl. III. Fig. 16).

Along one side of the anterior portion of the small intestine the epithelial lining is thrown into numerous folds and grooves (Pl. III. Fig. 16, T. R.). Hamilton (11) has referred to this in *Nepa* as the "pigmented streak". It is at this region the hind-gut runs into the mid-gut as shown in serial sections. The peculiar epithelium of this region therefore represents a transition between the small intestine and the mid-gut.

THE RECTAL CAECUM. A very thin-walled large sac filled with liquid contents is conspicuous on dissecting a fresh specimen of the insect. This is the rectal caecum which extends from the hind region of the abdomen right upto the thorax when fully distended. The liquid is sometimes clear but at other times it is of a dark colour with suspended granules. The histological structure of the epithelial lining of the caecum (Plate III. Figs. 17 and 18) shows numerous folds and grooves and resembles somewhat the epithelium of the transitional region described above. The cells have small oval nuclei. The wall is bounded by prominent strands of muscle fibres, the inner circular and the outer longitudinal, arranged in regular rows which in preparations of the entire caecum give a checkered appearance to the wall. The structure of the caecum of *Sphaerodema* does not resemble that of the caecum of *Nepa* as described and figured by Hamilton. She describes the muscular wall as possessing an inner layer of longitudinal and an outer layer of circular muscles, which is opposite to what we find in *Sphaerodema*.

In a living insect the caecum is found to contract rhythmically once for every two beats of the heart. This regular rhythmic movement naturally suggests a respiratory or circulatory function. Many previous investigators have tried to explain this action of the caecum in other aquatic bugs. But none has so far been able to do so satisfactorily. There is no doubt that the caecum is somehow correlated with the aquatic habits of the insect, as it is found only in aquatic species of the Hemiptera. Poisson (26) allotted a hydrostatic function to it, while Portier (27) suggested that it functioned as a "lavage rectale", an adaptation to aquatic life. But these suggestions do not explain the very regular contractions that the caecum presents. Poisson also suggested another function, that of a defensive organ. It is true that the insect ejects a jet of liquid at times when disturbed, but that occurs very rarely and it does not account for its regular contractions.

The tracheal supply is not such as would suggest any direct respiratory function like that of a tracheal gill. The thin membranous wall of the caecum may help to diffuse oxygen from the water in the caecum into the blood in the haemocoel. The rhythmic action may produce a current of water in and out of the caecum and may make such a diffusion of gases possible. An inward current of water has not however been noticed and as such it does not seem to be its correct function.

In another way the caecum may help respiration, as we have suggested in another paper (29). Its rhythmic contractions may be a contrivance to ventilate the tracheal trunks and be a more efficient one than the beating of the heart or the peristalsis of the alimentary canal.

THE RECTUM. The rectal portion of the alimentary canal is similar in appearance to the caecum. But transverse sections reveal that the dorsal half of its wall bears the structure of the small intestine while the structure of the ventral half is like that of the caecum. A section through the junction where the small intestine passes into the caecum is shown in Plate III Figure 19.

THE SALIVARY GLANDS. A pair of salivary glands lies in the anterior region of the thorax. Each gland is composed of a main salivary gland, a subsidiary salivary gland and the so-called receptacle. The main gland (Text Fig. 15) is an elongated organ made up of numerous small rounded lobes or acini arranged round a central duct. The acini are smaller towards the distal end of the gland. At the proximal end of the main gland is a large bilobed thin-walled sac containing a milky fluid. It is easily burst open at the slightest touch, and the fluid flows out. As the fluid is saliva this sac probably functions as a salivary receptacle. The subsidiary gland is similar though much smaller than the main gland, and its component acini are also smaller than those of the latter. Besides, the subsidiary gland does not possess thin walled sac at its anterior end like the one present on the main gland. A short duct issues out of the subsidiary gland and opens into the sac of the main gland. A small flattened oval organ the so-called receptacle, lies a little behind the main gland. Its long narrow duct runs forward and curves back to enter the sac of the main gland at the point where the duct of the subsidiary gland enters. It is not certain if this organ really serves as a receptacle. The salivary duct issues out of the main gland and continues upto the head where it unites with its fellow of the opposite side before opening into the base of the salivary syringe.

Transverse sections of the glands are shown in Plate II Figures

8 and 9. Each acinus is a single large cell having a peripheral protoplasmic region with two or three large nuclei and a large central vacuole containing the secretion of the cell (Plate II. Figs. 11 and 12). The secretions of the two glands seem to be different. It is so also in *Nepa* and from the nature of these secretions Hamilton (11) suggests that they may combine to produce a reaction similar to that of the acid and alkaline secretions of the poison glands of the wasps, etc. The secretions of the two glands do mix in the two white lobes at the anterior end of the main gland, and there is a common duct which carries the saliva to the rostrum. The duct is made up of a single layer of small cubical cells (Pl. II. Fig. 10.)

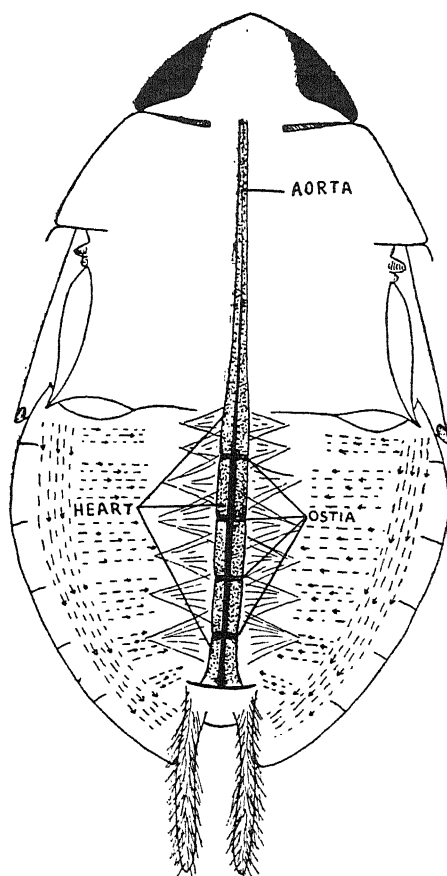
THE MALPIGHIAN TUBULES. The malpighian tubules (Text Fig. 15) appear to be four in number but a closer examination reveals that as in *Nepa* they are only two very much coiled long narrow tubes which open into the alimentary canal at the "pyloric collar" by both their ends. In transverse section (Pl. II. Fig. 7) a tubule is found to be made up of a single layer of large epithelial cells with large oval nuclei. On the internal and external borders of each cell are marked out narrow zones of striations representing the pore canals and canaliculi. A peritoneal membrane surrounds the tube.

VII. THE CIRCULATORY SYSTEM

THE DORSAL VESSEL. The dorsal blood vessel is distinguished into a thick-walled heart lying in the abdomen and a narrow thin-walled aorta in the thoracic region (Text Fig. 16). Four pairs of ostia divide the heart into five chambers. Anteriorly it narrows into a thin vessel, the aorta, which terminates in the head. The heart lies in the dorsal sinus suspended from the abdominal terga. Seven pairs of alary muscles are attached to the heart. Rhythmic contractions of the heart take place in a flowing movement from behind forward pumping the blood in a forward direction. In the tibiae of all the legs are noticed secondary pulsating organs which aid the circulation of blood.

THE BLOOD AND CIRCULATION. The flow of blood can be observed in a transparent living specimen in the abdominal region. Blood travels backwards in the margins of the abdominal cavity and in each segment some blood is diverted inwards, entering the heart through the ostia at every diastole. At systole, the blood in the heart is carried forwards through the aorta to the head sinuses. The blood has a greenish colour and the walls of the heart therefore appear green.

Muttkowski (21) demonstrated the presence of a respiratory protein with a copper nucleus, in the blood of insects. To insect



Text Fig. 16—The Circulatory System. Arrows show the circulation of blood in the abdominal cavity.

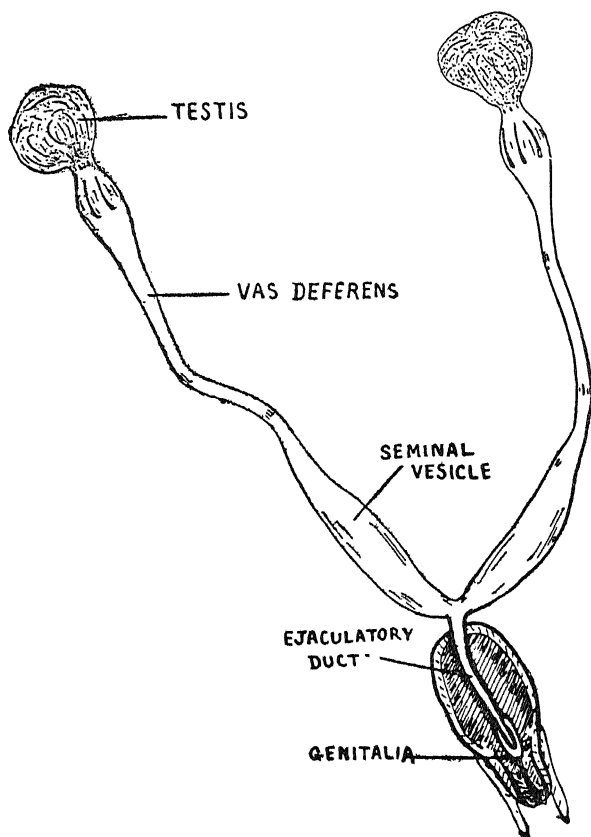
blood, which has hitherto been regarded as having nothing to do with respiration, has thereby been attributed a respiratory function also.

VIII. THE REPRODUCTIVE SYSTEM

The sexes are similar in external appearance and it is very difficult, though not quite impossible, to distinguish a male from a female, on superficial examination. The only sign of distinction is the slightly more bulged out abdomen of the female. But a female

bearing eggs has a conspicuously bulged abdomen and the eggs inside can be readily made out through the transparent body wall.

THE MALE REPRODUCTIVE ORGANS. The testes (Text Fig. 17) are rounded bodies each composed of a tangle of five seminal tubules lying ventrally in the lateral region of the third abdominal segment. They are richly supplied with tracheoles from the short second spiracular tracheae of the abdomen. The seminal tubules are enclosed in a single scrotum and can be separated out by tearing open this investing membrane.



Text Fig. 17—The Male Reproductive System. $\times 11$.

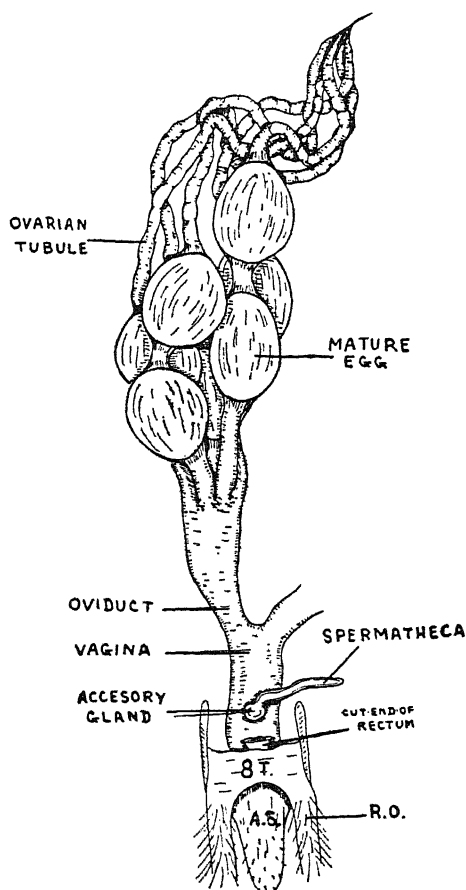
The two vasa deferentia unite posteriorly to form the narrow ejaculatory duct which leads into the aedeagus. The posterior parts of the vasa deferentia are enlarged to function as vesicula seminalis.

The male organs of *Sphaerodema* differ from those of *Nepa cinerea*, in which the vasa deferentia are long, narrow, much coiled

tubes and at the base of each opens a coiled seminal vesicle (vide Hamilton.) In *Ranatra fusca*, according to Marshall and Severin (vide Imms (14) p. 342.), the two vesicula seminales are as in *Sphaerodema* simply the enlarged posterior parts of the vasa deferentia. The seminal tubules are however six in number in that insect.

The seminal tubules, vasa deferentia and seminal vesicles contain masses of coiled spermatozoa with very long tails (Pl. II. Fig. 3.)

THE FEMALE REPRODUCTIVE SYSTEM. Each ovary (Text Fig. 18) is made up of five long thin-walled ovarian tubules or ovarioles which extend right upto the prothorax. The ovaries like the testes are also supplied with numerous tracheoles from the second spiracular tracheae. The free fine ends of the ovarian



Text Fig. 18—The Female Reproductive System. $\times 11$.

tubules unite into a fine terminal filament. Posteriorly the five tubules open into a broad egg calyx which receives the ripe eggs before they pass into the oviduct which is very short. The oviducts of the two sides unite to form the median vagina. Dorsal to the vagina is situated a small elongated sac, the spermatheca. Posterior to the opening of the spermatheca and very close to it is a small round accessory gland.

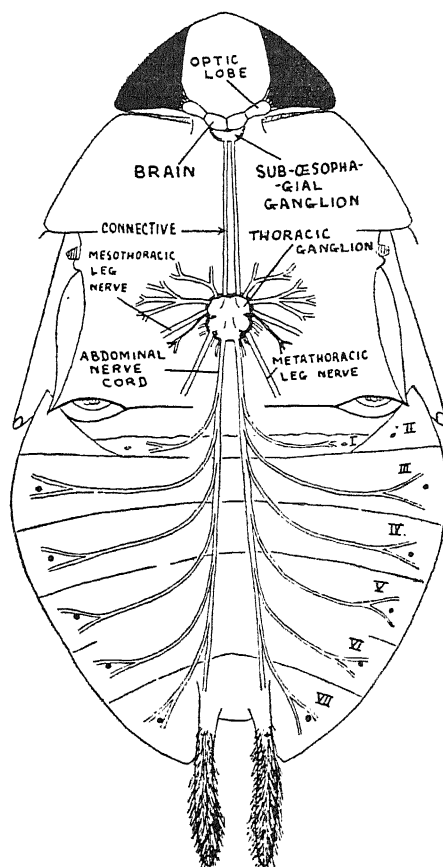
Each ovariole is divided into three regions: (1) the terminal filament which unites with the others and attaches the ovary to the prothorax; (2) the terminal chamber or germarium with undifferentiated cells; and (3) the posterior main division, the vitellarium, containing the developing and ripe eggs. The last portion is constricted into a number of follicles, each of which contains a single ovum. This gives the ovariole a beaded appearance. The ovarioles are typically Rhynchotan being of the acrotropic type carrying the nutritive cells in the terminal chamber.

Plate II Figure 4 is a transverse section through a follicle showing a large ovum surrounded by small follicle cells. Plate II Figure 5 is a transverse section of the anterior portion of an ovariole with young developing ova surrounded by follicle cells. The oviduct is made up of a single layer of small epithelial cells and two layers of muscles, the inner longitudinal and the outer circular (Pl. II. Fig. 6).

IX. THE NERVOUS SYSTEM

The concentration of the nervous system (Text Fig. 19) in *Sphaerodema* is like that in *Nepa*. All the ventral ganglia are fused together in two masses situated in the thorax. The first of these is situated almost in the neck region and is formed by the fusion of two ganglia—the suboesophageal and the prothoracic. This we shall refer to as the suboesophageal ganglion. The other lies in the posterior region of the mesothorax and is a composite of the mesothoracic, the metathoracic and all the abdominal ganglia. This will be referred to as the mesothoracic ganglion. The brain lies immediately above the suboesophageal ganglion and is connected to it by two very short, stout connectives, leaving a small opening for the oesophagus to pass through. A double connective joins the suboesophageal ganglion to the mesothoracic ganglion. From the latter two ventral nerve cords run into the abdomen. Apparently two stout nerves proceed to the last segment of the abdomen giving out branches to the abdominal segments. But actually these two are made up of several fine nerves which run together in two bundles. The outermost of these nerves run with

the bundles only upto the first abdominal segment and then separate out to supply the first two abdominal segments. Each succeeding segment is supplied with a pair of nerves which separate out of these bundles at regular intervals.



Text Fig. 19—The Nervous System.

THE BRAIN. The small bilobed brain lies in the posterior-most region of the head, almost in the neck. It bears on the sides two optic lobes which are slightly smaller in size than the lobes of the brain. The optic lobes give out a number of fine nerves to the eyes. From the brain a pair of nerves are supplied to the antennae. In sections the brain shows two distinct regions—the outer cellular region made up of ganglion cells, and the central medulated region made up of fine fibres and a granular substance. The mushroom bodies found in more intelligent insects like the honey-bee are (as in *Nepa*) absent in *Sphaerodema*.

THE SUBOESOPHAGEAL GANGLION. The suboesophageal ganglionic mass, made up of the suboesophageal and the prothoracic ganglia, is a pear-shaped body lying close below the brain in the neck and is connected to the brain by short stout connectives. The connectives are so short that the whole mass appears as one with a small opening for the oesophagus to pass through. Three pairs of nerves are given off anteriorly by the suboesophageal ganglion to the mouth parts. From the posterior portion of the ganglion arises a pair of nerves which supplies the prothoracic legs. Two stout connectives running posteriorly join the mesothoracic ganglion.

THE MESOTHORACIC GANGLION. Three distinct regions can be marked out in this ganglionic mass; the anterior region represents the true mesothoracic ganglion, the middle region the metathoracic, and the posterior region represents the abdominal ganglia, as these supply nerves to the respective parts of the insect.

From the anterior region four nerves arise on each side. The first divides into two and supplies the ventral anterior region of the mesothorax. The second runs laterally to the wing and the leg muscles of the mesothorax. The third is stouter than the first two and supplies the mesothoracic legs. Another very slender nerve has its origin near the last one. The middle region of the ganglion gives out three pairs of nerves. The first two of either side are very fine and they innervate the muscles of the metathorax. The third is a stout nerve which goes to the metathoracic leg. The posterior region of the ganglion sends out a number of fine nerves. The first two pairs are distinct; the others unite to form the two ventral nerve cords. These bundles originate close together from the posterior end of the ganglion and diverge to the hind end of the abdomen. A pair of nerves runs out from the bundles in each of the visible abdominal segments and a pair is supplied to the anal and genital segments. These individual nerves can easily be separated from the bundles right upto the ganglion, thus indicating their independent entity.

THE TRACHEAL SUPPLY OF THE NERVOUS SYSTEM. The tracheae not only supply oxygen to the nervous tissue but also keep the ganglia in their places. The main tracheal trunks enter the head and give out branches to the brain. A pair of diagonal tracheae in the prothorax forms a cross below the suboesophageal mass and from these, tracheoles penetrate into the ganglion. Similarly a pair of diagonal tracheae in the mesothorax forms a cross ventral to the mesothoracic ganglion and send out tracheoles to the anterior ventral region of the ganglion and to the anterior

nerves. From the posterior end of the cross a pair of tracheae ramifies into the dorsal anterior region of the ganglion. The transverse ventral trachea of the mesothorax interlaces with the posterior portion of the ganglion and the nerves of that region. It sends out a pair of ramifying tracheae to the ventral posterior side of the ganglion, and another pair to the dorsal side, and tracheoles to the various nerves. The ventral commissural tracheae of the abdomen supply tracheoles to the abdominal nerves.

THE SENSE ORGANS. Scattered on the body of the insect are found rounded disc-like specialisations of chitin. These are innervated by nerves and are to be regarded as sensillae. They are of general occurrence in the Rhynchota. They show some variations in their shape and arrangement in the different families. Their nature and distribution might be of taxonomic value. Besides these there are short stout sensory spines on the legs, on the margins of the abdomen, on the margins of the air-flaps, etc. These spines show longitudinal ridges. A third kind of sense organs found in this insect are long fine bristles or hair also found on the legs and air-flaps etc. Flattened sense scales described by Hamilton in *Nepa* are wanting in *Sphaerodema*. It is doubted whether the flattened scales noted by her are only the sensillae described above. We have not found any scaly nature in these sensillae.

X. SUMMARY

1. The general habits and life-history of the bug are given.
2. The morphological structures of the head, the thorax and the abdomen, and their appendages are described in detail.
3. Certain endotergites are absent in the degenerate winged form. These endotergites are those used for the attachment of the dorso-longitudinal indirect wing muscles in the normal winged form.
4. The tarsi of the second and the third pair of legs are three-jointed in the adult and not two-jointed as described by Distant.
5. The sides of the eighth abdominal segment are prolonged into strap-shaped organs which are retractile. They carry the last pair of spiracles on their bases. The development of these organs is noted. These organs are found to be homologous and analogous to the respiratory siphon of the *Nepidae*.
6. The anatomy of the digestive, circulatory, reproductive and nervous systems is worked out and the histological structures of the various organs are given.

7. To the prominent rectal caecum found in *Sphaerodema* and other aquatic bugs is ascribed the function of ventilating the tracheal trunks. This has been suggested on account of the rhythmic contractions it manifests.

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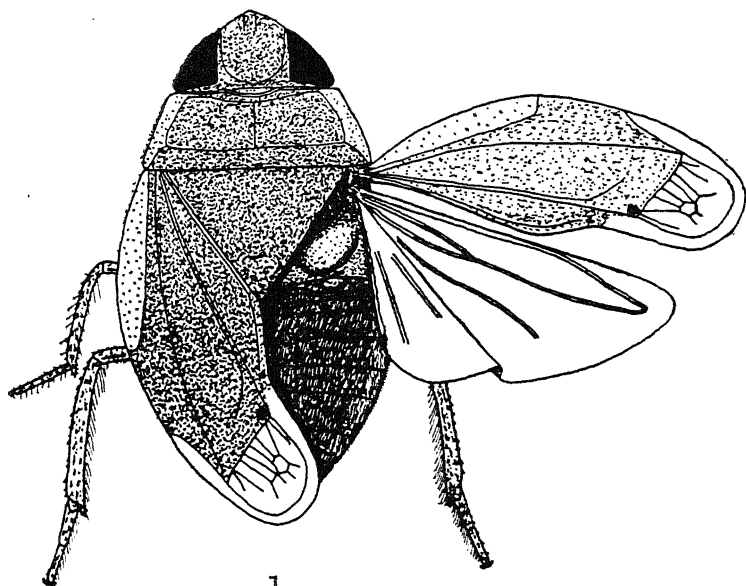
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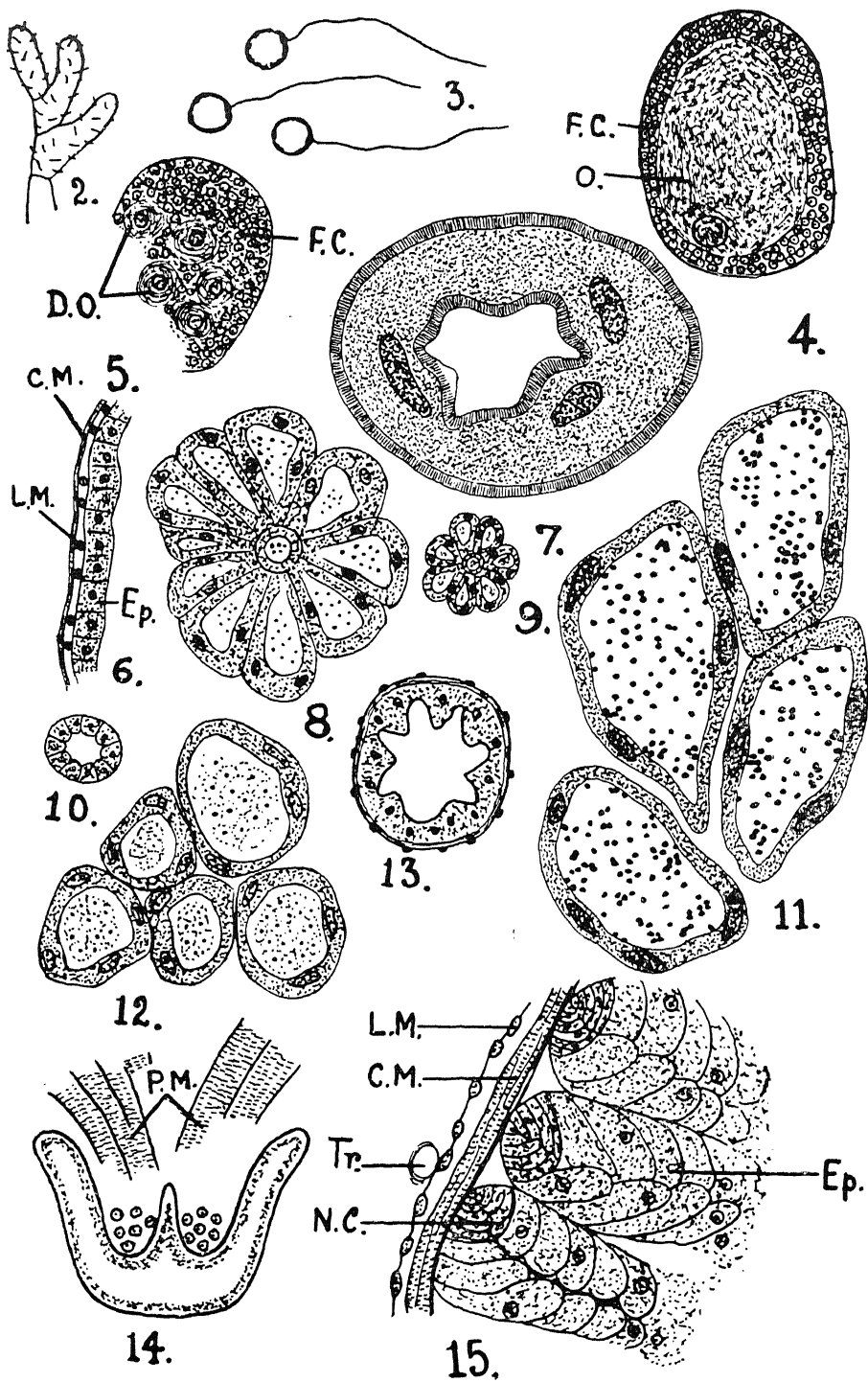
XII. EXPLANATION OF THE PLATES

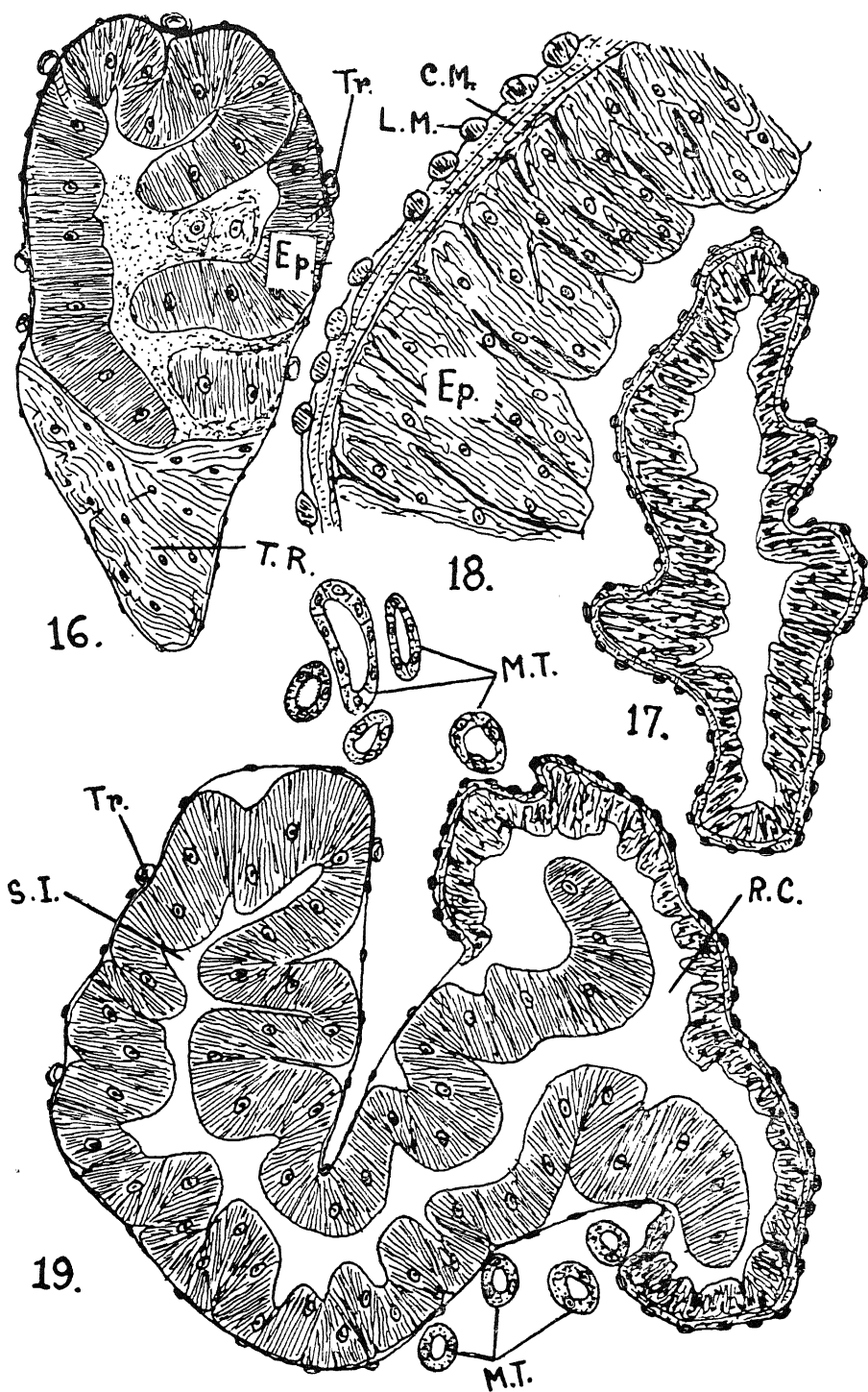
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|-----------|----------|---|
| Plate I | Fig. 1. | Dorsal view of adult <i>Sphaerodema</i> . |
| Plate II | Fig. 2. | Antenna. (X33). |
| | Fig. 3. | Coiled Spermatozoa from Seminal Vesicle (X700). |
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| | Fig. 12. | T. S. of Portion of Subsidiary Salivary Gland of Adult. (X150). |
| | Fig. 13. | T. S. of Oesophagus. (X700). |
| | Fig. 14. | T. S. of Pharynx. (X550). |
| | Fig. 15. | T. S. of Mid-gut. (X300). |
| Plate III | Fig. 16. | T. S. of Small Intestine. (X150). |
| | Fig. 17. | T. S. of Rectal Caecum. (X150). |
| | Fig. 18. | T. S. of Portion of Rectal Caecum highly magnified. (X550). |
| | Fig. 19. | T. S. of Hind-gut Showing Small Intestine Opening into the Rectal Caecum. (X. 150). |

Presswalla & George Plate I



1.





LETTERINGS

| | |
|--------------|--|
| I—IX | Abdominal Segments 1 to 9. |
| 1st Abd. Sp. | First Abdominal Spiracle. |
| 8th Abd. Sp. | Eighth Abdominal Spiracle. |
| Aed. | Aedeagus. |
| A. O. L. | Anterior Ovipositor Lobe. |
| A. S. | Anal Segment. |
| Br. | Brain. |
| C. M. | Circular Muscle. |
| C. S. F. | Chitinous Support of Female genitalia. |
| C. S. M. | Chitinous Support of Male genitalia. |
| D. O. | Developing Ova. |
| D. S. | Dorsal Spines. |
| E. | Eye. |
| Ep. | Epithelium. |
| F. C. | Follicle Cells. |
| I. O. | Intromittent Organ. |
| I. O. L. | Inner Ovipositor Lobe. |
| L. M. | Longitudinal Muscle. |
| L. O. L. | Lateral Ovipositor Lobe. |
| L. P. | Lateral Plate of Aedeagus. |
| Md. L. | Mandibular Lever. |
| Md. S. | Mandibular Stylet. |
| Ms. G. | Mesothoracic Ganglion. |
| Ms. Sp. | Mesothoracic Spiracle. |
| M. T. | Malpighian Tubules. |
| Mx. S. | Maxillary Stylet. |
| N. C. | Nest Cells. |
| O. | Ovum. |
| Oe. | Oesophagus. |
| O. L. | Optic Lobe. |
| Par. | Paramere. |
| P. M. | Pharyngeal Muscle. |
| R. C. | Rectal Caecum. |
| R. O. | Retractile Organs. |
| 8S. | Eighth Sternum. |
| 9S. | Ninth Sternum. |
| Sub. Oes. G. | Sub-Oesophageal Ganglion. |
| S. P. | Salivary Pump. |
| 8T. | Eighth Tergum. |
| Te. | Tentorium. |
| Tr. | Trachea. |
| T. R. | Transitional Region. |
| V. S. | Ventral Spines. |

THE ALIMENTARY CANAL
OF
THALASSEMA BOMBAYENSIS (PRASHAD AND AWATI).
(With 15 Text-figures)

BY

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The alimentary canal in *Thalassema bombayensis* is a simple narrow tube more or less of a uniform diameter throughout its length. The tube is extremely elastic and gets distended a great deal when food-balls and pellets are passing through it.

The entire canal can be divided into three sections, of which the first and the last sections are almost straight while the middle section is very much complicated and thrown into several loops (Fig. 1).

Each section can further be divided into several parts. The first section beginning with the mouth consists of the pharynx, oesophagus, gizzard and the crop. The middle part which forms a series of loops of successively longer lengths consists only of the intestine which is conveniently subdivided into three parts irrespective of the loops: (a) the pre-collateral intestine (Zwischendarm); (b) the collateral intestine (Mitteldarm); and (c) post collateral intestine (Hinterdarm). Lastly the third section of the alimentary canal which is almost a straight short tube which becomes the rectum or the posterior part of the gut terminating into the anus.

The whole of the alimentary canal is attached to the body-wall by means of several mesenteries (suspensory ligaments), the most important among them being the dorsal mesentery which runs along the whole length of the dorsal surface of the gut except in the region of the pharynx, oesophagus and the gizzard on one hand and the distal part of the rectum on the other. The pharynx and the distal part of the rectum are on the other hand, attached to the body-wall by mesenteries radiating in all directions; while the oesophagus and the gizzard are bound to the ventral body-wall by a pair of sheets of the ventral mesenteries one sheet

on each side of the nerve cord. The portion of the alimentary canal immediately beyond the crop is slung to the body-wall by several mesenteries or ligaments running in different directions in addition to the dorsal mesentery as already mentioned above.

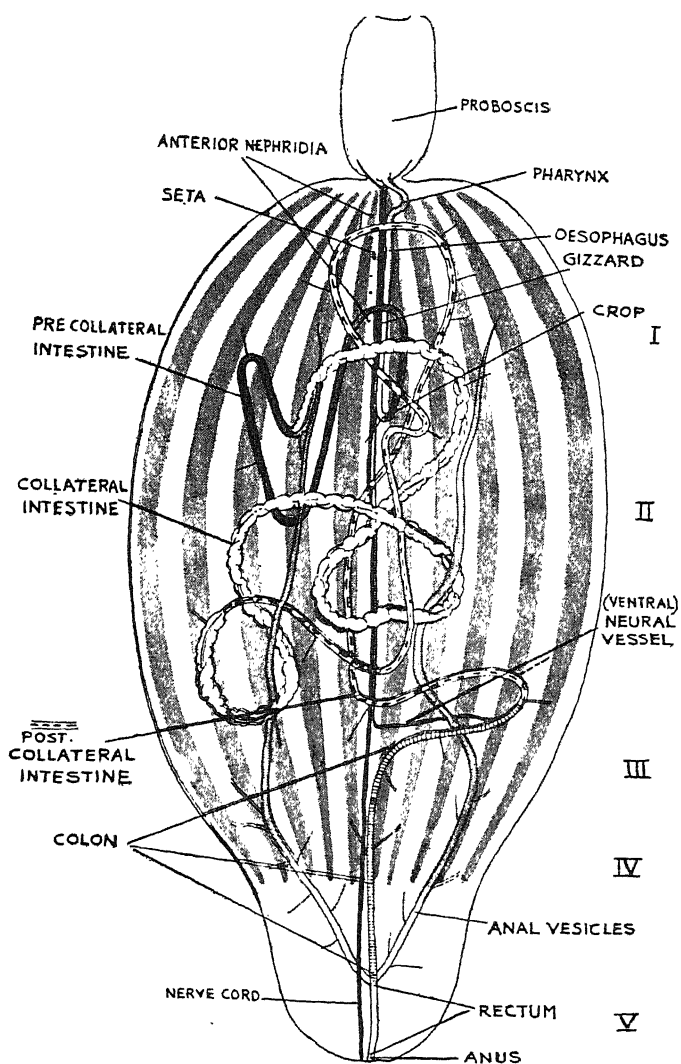


Fig. 1—Dissection of *Thalassema bombayensis* showing diagrammatically several loops of the alimentary canal. $\times 5$

I. THE FIRST SECTION OF THE ALIMENTARY CANAL

1. THE MOUTH. The mouth is situated more or less on the ventral side of the extreme anterior end of the animal at the base of the proboscis which surrounds the aperture and forms a sort of a funnel. The mouth is generally closed in preserved specimens and presents the star shaped appearance due to small furrows. It is surrounded by a strong sphincter muscle made up of broad bands of circular muscles.

2. THE PHARYNX. (Figs. 2 and 3). The mouth leads into a specious pharynx which is triangular in shape in a cross-section. Externally it is covered over by radiating mesenteric strands by means of which it is attached to the adjoining region of the body-wall. During its course the pharynx is bent a little upon itself.

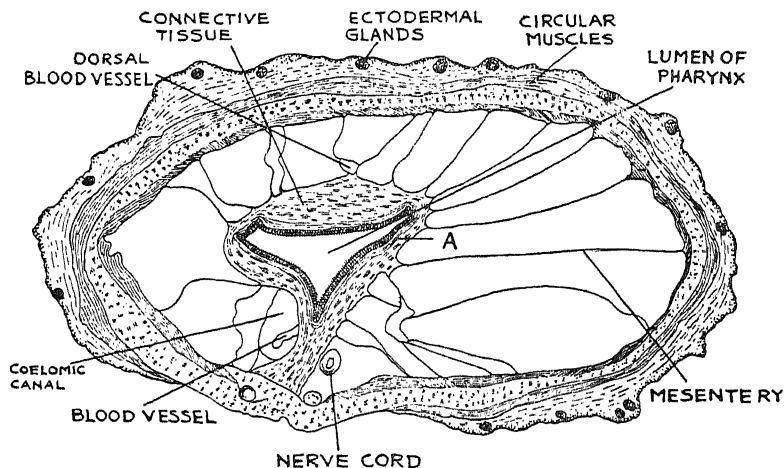


Fig. 2—A transverse section of the Pharynx. $\times 30$

Internally the wall of the pharynx shows a smooth lining, there being no ridges and furrows such as characterise the lining of the succeeding parts of the gut e.g. the oesophagus and the gizzard. In a series of transverse sections, the pharyngeal epithelium is seen to consist of tall cylindrical ciliated cells with the nuclei lying in the centre. The cilia are short and numerous. A few unicellular glands are found embedded in the epithelium and they presumably discharge their secretions into the lumen of the pharynx. The epithelium is surrounded on the outside by many layers of circular muscle fibres embedded in the connective tissue. The outer thick covering of the pharynx is formed by the

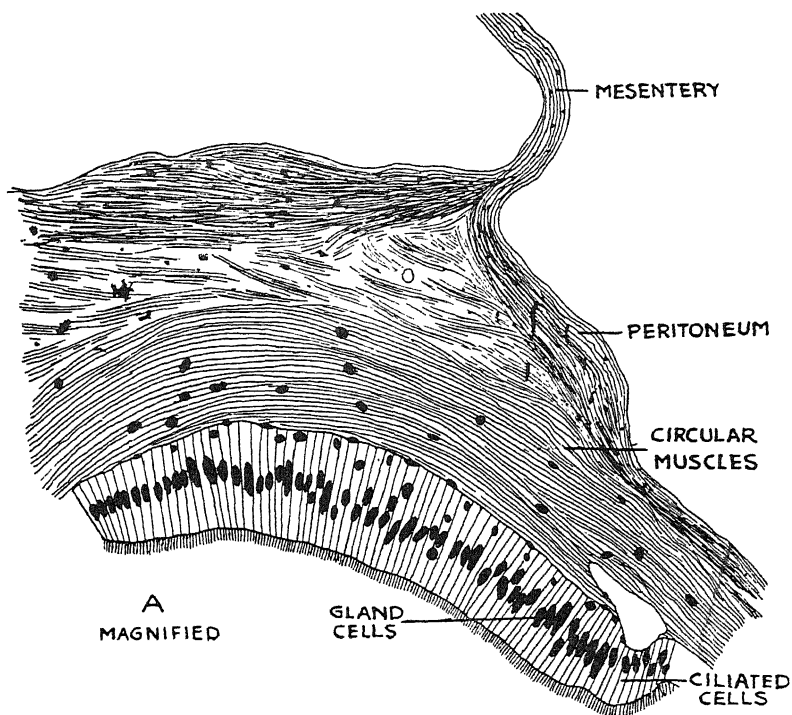


Fig. 3—A small part from Fig. 2 magnified $\times 240$.

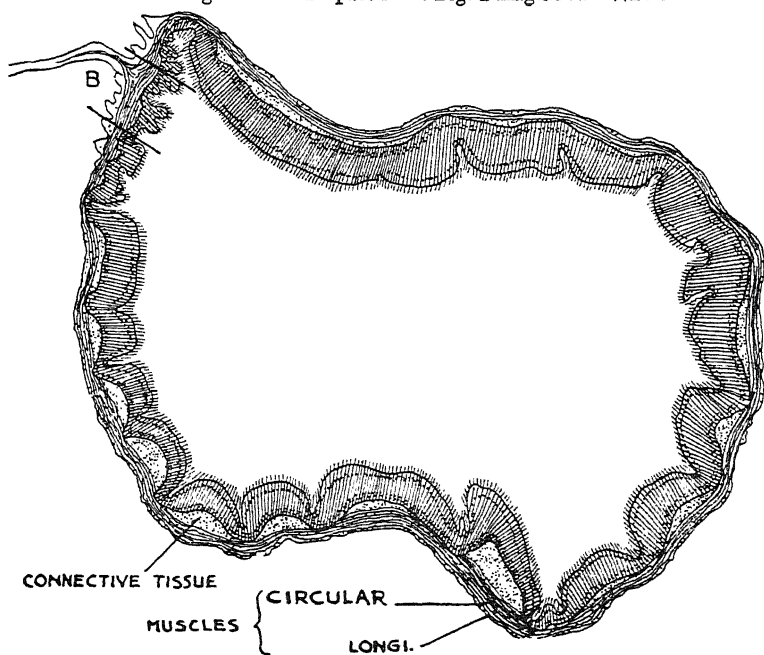


Fig. 4—Transverse section of the Oesophagus. $\times 50$.

peritoneal lining which is continued towards the body-wall in the form of numerous mesenteric strands. The latter consist of elastic fibres.

3. THE OESOPHAGUS. (Figs. 4 and 5). Immediately behind the pharynx, the oesophagus begins. Internally the triangular lumen of the pharynx gives place to an oval cavity, while the internal lining is raised into series of flat ridges separated by corresponding shallow grooves. Externally the radiating mesenteric bands of the pharynx give place to a pair of ventral mesenteries which bind the oesophagus to the ventral wall of the body. These ventral mesenteries are continued posteriorly right up to the junction of the gizzard with the crop.

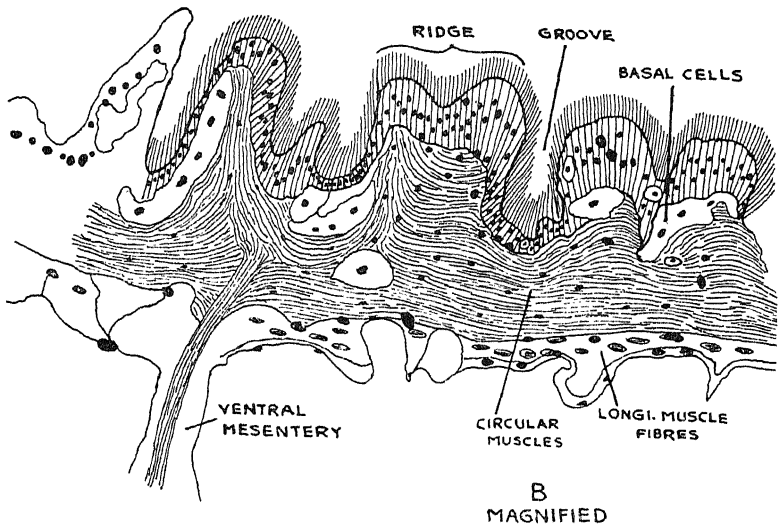


Fig. 5—Magnification of B in Fig. 4. $\times 240$

The oesophagus is the largest part of the canal in this section. Histologically the oesophagus presents several features which distinguish it from the pharynx. Each of the ridges is lined by tall cylindrical ciliated cells with many gland-cells, scattered among them; while the furrows are lined with cubical ciliated cells without any gland-cells (Fig. 5). The cilia arise from the distal thick walls of the columnar cells and are rather dense. The nuclei of these cells are located either near their distal ends or near their proximal ends so that there appear to be two rows of cells in the same epithelium (Fig. 5). This inner epithelium is surrounded on the outside by a thick layer of circular muscles which are in their turn covered over by a thin layer of longitudinal muscles. The peritoneal layer is, as usual, present on the exterior.

There is still another peculiar structure which is sometimes found at the base of the epithelial cells in the oesophagus. This structure consists of clear oval vacuoles with central nuclei. These vacuoles have been called by Spengel, "*Basal Cells*", while Jameson considers them as initial stages in the development of glandular cells. They are generally found near the attachment of a mesentery (Fig. 5).

4. THE GIZZARD. (Figs. 6 and 7). The oesophagus is followed by the gizzard, which is distinguished externally by its smooth glistening appearance.

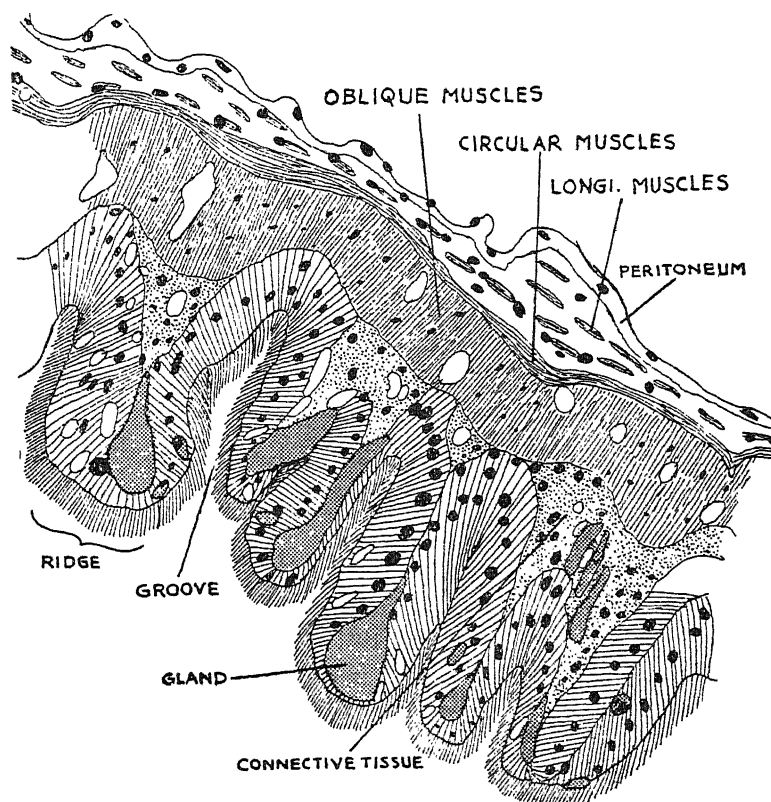


Fig. 6—A transverse section of the Gizzard. $\times 250$

Owing to the great development of the muscles on the inside, the wall of the gizzard appears to be thick. Internally some of the ridges are taller and more prominent and the grooves proportionally deeper. The gizzard is kept in position by the pair of the ventral mesenteries which are continued from those of the oesophageal region as flat membranes or sheets on either side of the nerve cord.

Histologically, the wall of the gizzard presents almost all the features of the oesophagus but there are a few differences. The lining epithelium consists of tall cylindrical cells with a double row of prominent nuclei : one row lying near the distal ends of the cells, while the other about the middle (see the oesophagus above).

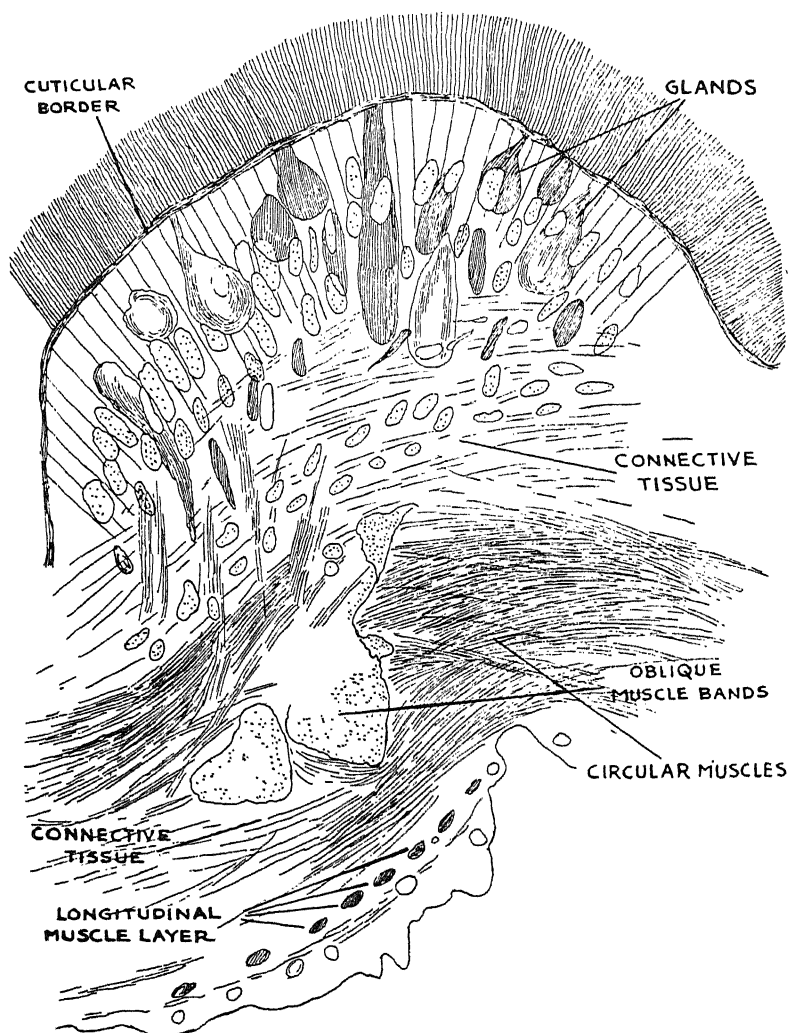


Fig. 7—A portion of the Gizzard magnified (oil immersion)

There are also many vacuoles which are found in between epithelial cells. These vacuoles may be representing glandular cells which have emptied their contents into the canal. The epithelial layer is surrounded by well-developed oblique muscles

which are covered externally by circular muscles. The longitudinal muscles are outermost and they do not form continuous but short separate bundles. Externally the gizzard is covered by a layer of the peritoneal epithelium.

A layer of fibrillar connective tissue similar to that of the oesophagus lies between the inner epithelium and the layer of muscle fibres.

Just before the gizzard opens into the crop, the characteristic ridges and furrows of the typical gizzard area disappear. This part forms a transitional area between the gizzard and the crop.

5. THE CROP. (Fig. 8 A and B). There are many important structural changes in the crop behind the gizzard. The ventral

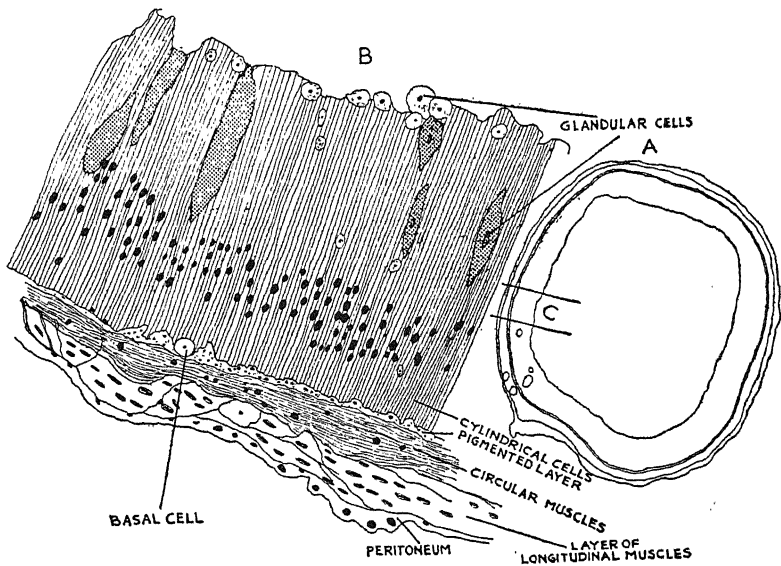


Fig. 8—A, Outline of a transverse section of the Crop. $\times 15$
B, Magnification of the portion C in A. $\times 150$

mesenteries disappear while the dorsal mesentery makes its first appearance and is found attached all along the dorsal surface of the crop. In between the double fold of this mesentery is found the dorsal blood vessel. This mesentery which runs towards the anterior end parallel with the dorsal blood vessel, attaches firmly the crop to the dorsal body-wall. The crop is surrounded on the dorsal side at its posterior end by an incomplete vascular ring formed by two transverse loop vessels opening into each other and into the dorsal vessel.

Externally the crop is not so smooth and glistening as the

gizzard. Internally there are also many important changes. The longitudinal ridges and grooves of the gizzard and the oesophagus disappear completely and in their place is found a more or less smooth lining of cells with an even surface. In some specimens longitudinal ridges and grooves are very faintly seen, while in others transverse ones are faintly marked. These facts seem to show that these faint ridges and grooves are due to contractions due to peristalsis at the time of fixing the animal.

Histologically the crop presents a very characteristic appearance. The epithelium consists of very tall cylindrical cells which are compactly arranged in tiers one above the other. This arrangement gives a stratified appearance to an inner epithelium. This appearance is probably due to the fact that these tall cylindrical cells are cut in transverse sections at different levels and they therefore, seem to show the stratified appearance (Fig. 8 B).

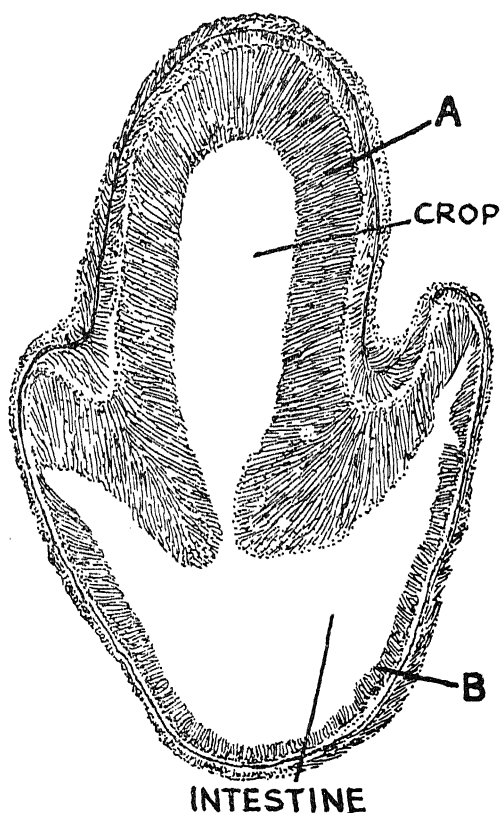


Fig. 9—A semi-diagrammatic figure of Sleeve Valve. $\times 36$

These cylindrical epithelial cells are not ciliated and this fact alone distinguishes the epithelium of the crop from that of the anterior regions of the alimentary canal. In *Thalassema bombayensis* the gland cells do not appear to be so well developed as they are in the case of *Thalassema neptuni* which have been described at great length by Jameson.

At places are found certain pigmented structures in a diffused state in between the layers of the epithelial cells and circular muscles. At other places clear cells each with the central nucleus, are seen at the base of the epithelium and are therefore known as basal cells.

The circular muscles are well developed and form a conspicuous and compact band round the inner epithelial lining. The longitudinal muscles are loosely arranged in bands across the vacuolar space which is bounded externally by the peritoneal membrane.

Towards the posterior end, the crop diminishes in size and passes into the intestine. At the junction of the crop with the intestine appears to be a valve which may be called a "Sleeve valve," because it forms a sleeve-like projection of the posterior extremity of

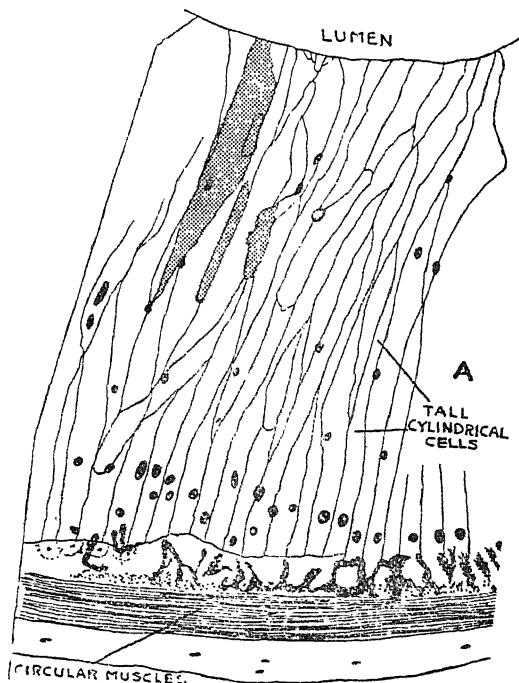


Fig. 10—A portion A in fig. 9 magnified. $\times 220$

the crop into the lumen of the anterior part of the intestine. This projected portion of the crop is of a double nature and its outer layer is continued on and becomes the epithelial lining of the intestine (Fig. 9).

Externally this valve is indicated by a conspicuous constriction to which Jameson has given the name of the "Preintestinal constriction". He does not, however, refer to this valve or any other valve in *Thalassema neptuni* at this place.

The structure of the valve can be easily understood from a longitudinal section of this region. The base of the valve is filled with muscles which are largely drawn from the layer of the circular muscles of the crop. This valve has two kinds of epithelia. One of the crop and the other of the intestine. The former consists of taller cells while the latter of short cylindrical cells (Figs. 10 and 11).

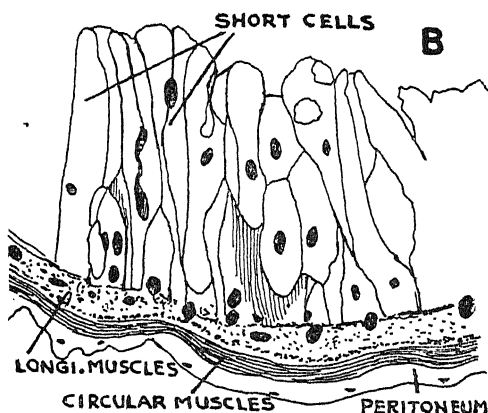


Fig. 11—A portion B in fig. 9 magnified. $\times 340$

II. THE MIDDLE SECTION OF THE ALIMENTARY CANAL

The parts of this section, as already mentioned above, are thrown into several loops of various lengths. These parts are characterised by the presence of a uniform epithelium consisting of more or less tall cylindrical cells loosely arranged, almost complete absence of the ciliated epithelium except in the beginning and the end of the Nebendarm, the presence of a continuous band of fibres of longitudinal muscles on the ventral side except in the regions of the Magendarm and Nebendarm, the presence of the dorsal mesentery and lastly by reversed arrangements of the layers of muscles surrounding the epithelium i. e. in the first section of the alimentary canal the circular muscles are

internal and are surrounded on the outside by the longitudinal muscles when present; while in this section the longitudinal muscles are internal and the circular are on the outside (Figs. 10 and 11).

In the place of the ventral muscular bands, Jameson has, however, described in *Thalassema Neptuni* a ciliated groove throughout this section. This ciliated groove in the regions of the Magendarm and Nebendarm is merged into the collateral stomach. In the present animal it seems to be entirely absent since the examination of many series of sections, several dissections and a few preparations of whole mounts have failed to reveal the presence of this ciliated groove. There are no cilia in any other regions except at the beginning and the end of the collateral stomach.

1. The Precollateral intestine (Zwischendarm) begins from the posterior end of the sleeve-valve, and forms approximately two loops. The dorsal mesentery which is a continuation of that of the crop, shows at its base a conspicuous intestinal sinus, since in a living animal there is a conspicuously coloured streak along the base of this mesentery. It may be, therefore, presumed that there is a series of sinuses at the base of the mesentery. It is in this region that faecal pellets are beginning to be formed and are, therefore, seen for the first time. The shorter of the two loops crosses the first sections of the canal in the region of the gizzard or the posterior part of the oesophagus, while the second which is longer, lies on the dorso-lateral side of the animal. Both the parts are attached all round to the body wall by narrow strips of suspensory ligaments in addition to the dorsal mesentery.

2. The collateral intestine (Mitteldarm) consists of two tubes of unequal dimensions situated dorso-ventrally. The dorsal tube (Magendarm) is bigger of the two with a wider lumen, while the ventral (Nebendarm) is very much smaller with a narrower lumen (Fig. 12).

The ventral tube (Nebendarm) is formed from the ventral part of the dorsal tube and its lumen is continued from that of the latter. At its beginning and its end it is lined with the columnar ciliated cells with prominent nuclei in the centre. The ciliated epithelium is not, however, found in the mid-portion of the Nebendarm (Fig. 13).

A series of transverse sections of the mid-portion of this part shows that the epithelia of the dorsal as well as of the ventral tube consists of tall cylindrical cells with nuclei irregularly scattered, though many of them are found located nearer the base. The epithelia are surrounded by well developed fibres of longitudinal muscles which are covered over their external sides by a layer of

weakly developed circular muscles. The peritoneal layer is found on the outside of these muscles. There are also basal and gland cells (Fig. 12).

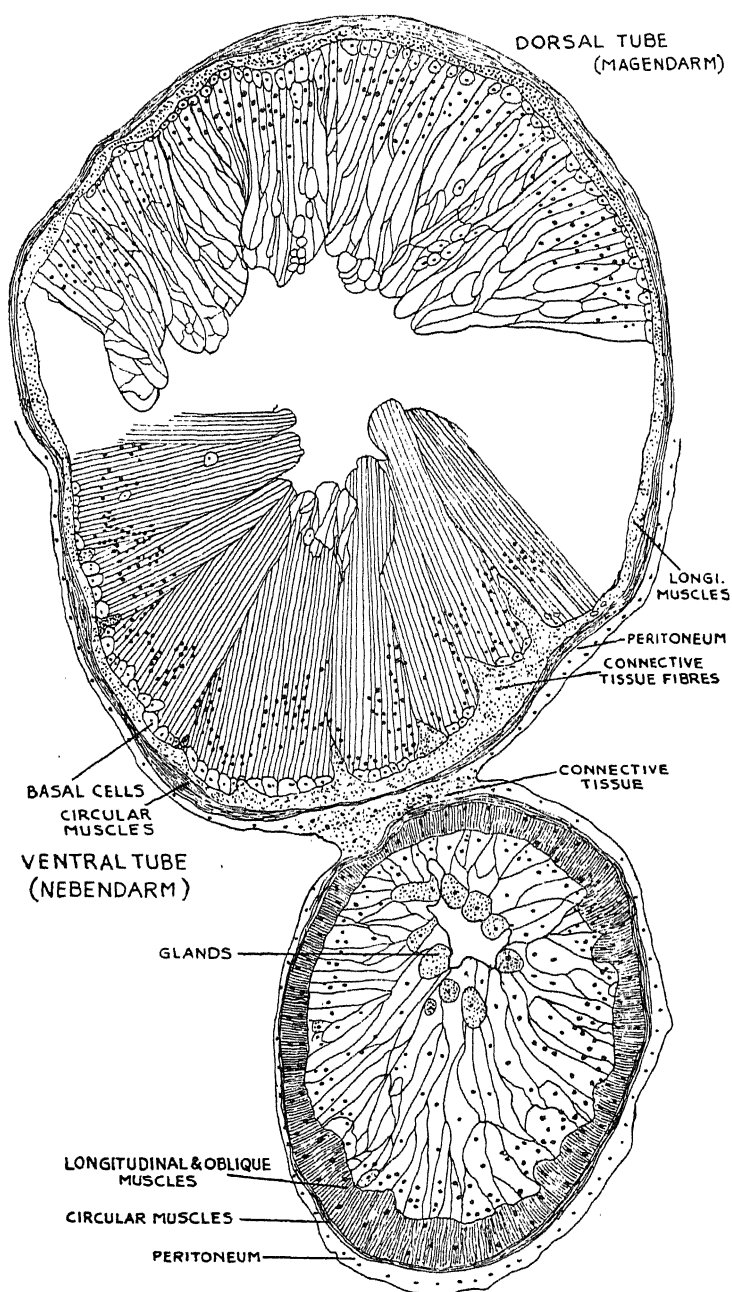


Fig. 12—A transverse section of the Mitteldarm. $\times 96$

There are, however, certain differences in the histological structures of these two tubes. In the dorsal tube the basal cells are very well developed at the base of the epithelial layer, while they are entirely absent in the ventral tube. Secondly the longitudinal muscles in the ventral tube are much more strongly developed than in the dorsal tube. Thirdly there are prominent glandular cells in the neighbourhood of the lumen of the ventral tube while they are not so prominent in the dorsal tube. And lastly there is a great development of the connective tissue in the dorsal tube so as to give an additional strength to the longitudinal muscles of the latter in order to drive out the faecal matter and sand particles. The collateral intestine undergoes a great deal of looping. Its extent can be easily understood from the figure (Fig. 1).

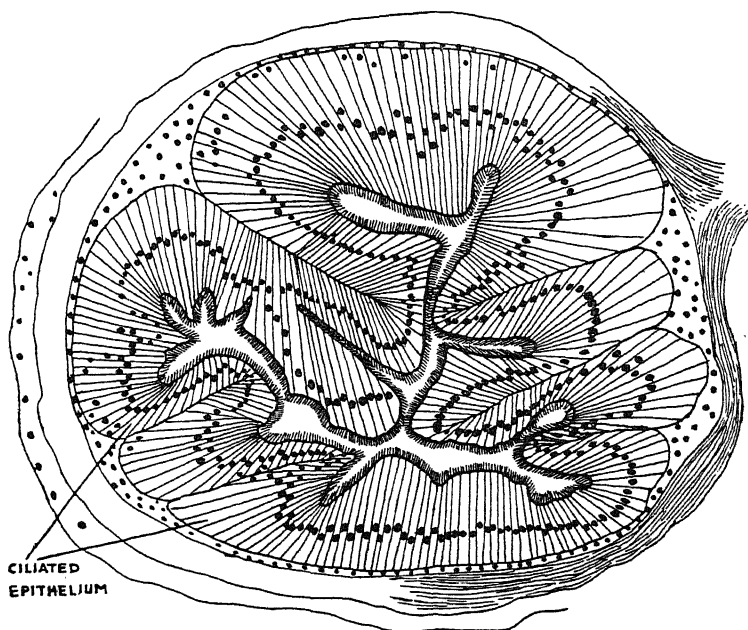


Fig. 13—Transverse section of the posterior end of the Nebendarm showing ciliated epithelial cells. $\times 210$

Function of the collateral stomach. The dorsal tube is generally filled with faecal pellets as well as sand particles. A current of water must therefore be obstructed while passing through it. Diverted through the ventral tube by the movement of the cilia found at its mouth, its continuous flow would be maintained by the movement of the cilia at the other end of the tube and also by the well developed muscles. This continuous current bringing in fresh water may be useful to the animal for respiratory purposes.

III. POST-COLLATERAL INTESTINE (HINTERDARM)

This structure begins from the place where the Nebendarm opens posteriorly into the alimentary canal and ends near about the region where the anal vesicles empty into it. According to Jameson, there is a little pouch or caecum at the end of this part of the alimentary canal which marks the beginning of the rectum in *Thalassema neptuni*. This caecum seems, however, to be absent in the present animal.

This part of the intestine can be divided into two portions not by any differences in the internal or external structures but by the fact that its proximal portion is looped while the distal is almost straight.

(1) The proximal portion which forms the last loop is always full of faecal pellets and is, therefore extremely distended. It is difficult on that account to make out its normal epithelial structures. The epithelial cells are either distorted when this region is empty or more or less of a cubical shape when it is stretched out. The arrangement of the muscles is rather perplexing. In some sections the layer of the longitudinal muscles seems to be surrounded by the circular muscles while in others of the same series the reverse is the case. As there are no intrinsic differences between the longitudinal and the circular muscles and the parts cut into sections are so mobile and elastic while living that it is possible that the sections of the same series may be cut along different planes and hence different pictures are to be seen in the same series.

(2) The distal portion forms the colon. *Thalassema bombayensis* seems to have no caecum as already mentioned above. In this region, however, the ventral (neural) vessel is attached to the ventral portion of the colon to which is generally found attached the genital stolon.

The distal part of the colon extends from the attachment of the genital stolon to the opening of the anal vesicles into the digestive canal. The epithelium is very irregular and consists of columnar or thread like cells, the free ends of which broaden out and merge into each other to form a pavement epithelium.

IV. END PARTS OF THE ALIMENTARY CANAL ARE:—

1. RECTUM OR CLOACA. (Figs. 14 and 15). The rectum or the cloaca is the last portion of the alimentary canal. In the whole of this region there are prominent longitudinal folds and grooves lining the lumen. The epithelium of these folds and grooves consists of low columnar or cubical cells which are

ciliated. Gland cells are also found scattered in the epithelium of the ridges. On the outside of the epithelium there are prominent bands of the circular muscles. Between the latter and the epithelium there is a connective tissue in which are found many gland cells, with very prominent nuclei. This glandular tissue has already been described by Rietsch, who has termed it as the peri-anal glandular organ. This tissue increases in extent towards the posterior end.

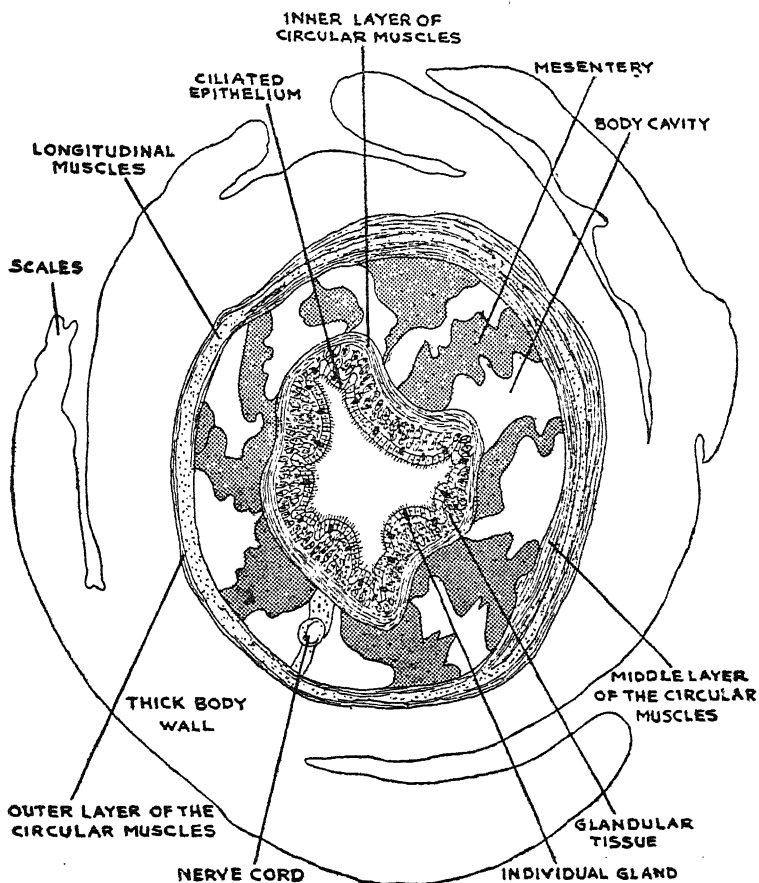


Fig. 14—T. S. of the posterior part of the body, passing through the rectum and showing the three layers of muscles. $\times 7$

The arrangement of the muscles varies considerably as one proceeds towards the posterior end of the animal. At the place where the anal vesicles open into the canal, there are three layers of circular muscles; the innermost lying on the top of the connective and glandular tissue, the middle layer lying outside the radial

mesenteries and surrounding the body cavity and lastly the outermost layer along the inner side of the body-wall below the peritoneum. The layer of longitudinal muscles which are very weakly developed is found between the middle and the outermost layers of the circular muscles (Fig. 14).

Towards the posterior end of the rectum certain important changes seem to occur in the arrangement of these muscles and the mesenteries. The latter have already disappeared or are fast disappearing while the innermost and the middle layers of the circular muscles are merging into each other to form one layer. Similarly the layer of longitudinal muscles is also disappearing. Ultimately a very big band of the circular muscles is thus formed by coalescence of all the three different layers with one another which will, later on, become the sphincter muscle (Fig. 15).

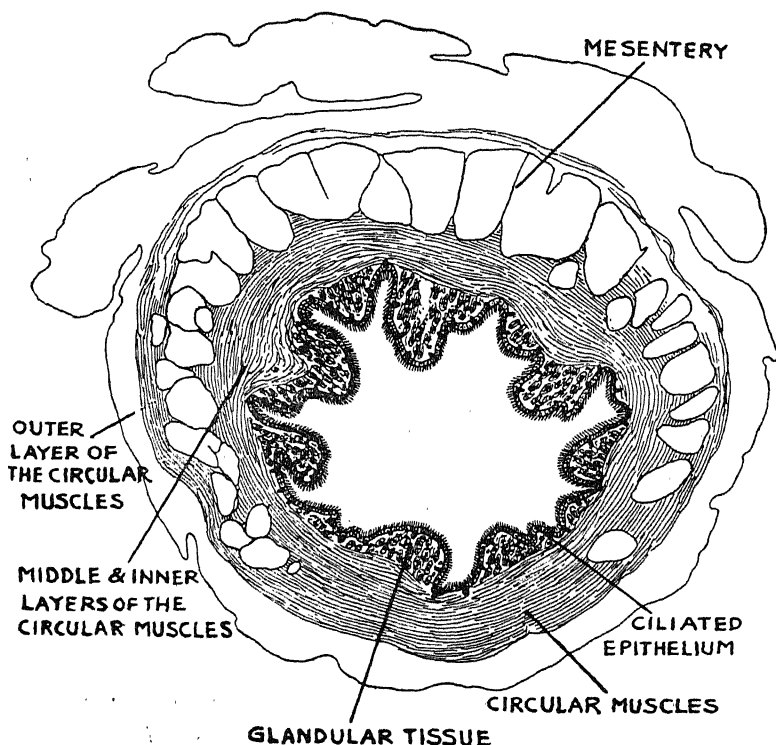


Fig. 15—Transverse section of the posterior part of the body passing through the Rectum and showing the three layers fusing into one. $\times 7$

The rectal portion should be termed the cloaca, since the anal vesicles which are the excretory organs of the animal open into

the last portion of the alimentary canal and the excretory and the rectal opening to the outside is common.

2. ANUS OR THE CLOACAL APERTURE. The anus is situated at the extreme posterior end of the animal. It has been noticed that water is continually forced out through the anus in a living animal. It is doubtful whether any water is taken in through the same aperture. The current of fresh water which enters the mouth, and is maintained by the ciliary movements of the cilia of the cells of the Nebendarm passes out at the other end through the anus so that a continuous current is kept up through the whole of the alimentary canal.

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A NEW GENUS AND SPECIES OF ZORAPTERA

BY

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(With 2 Text-figures)

MENONIA, GENUS NOV.

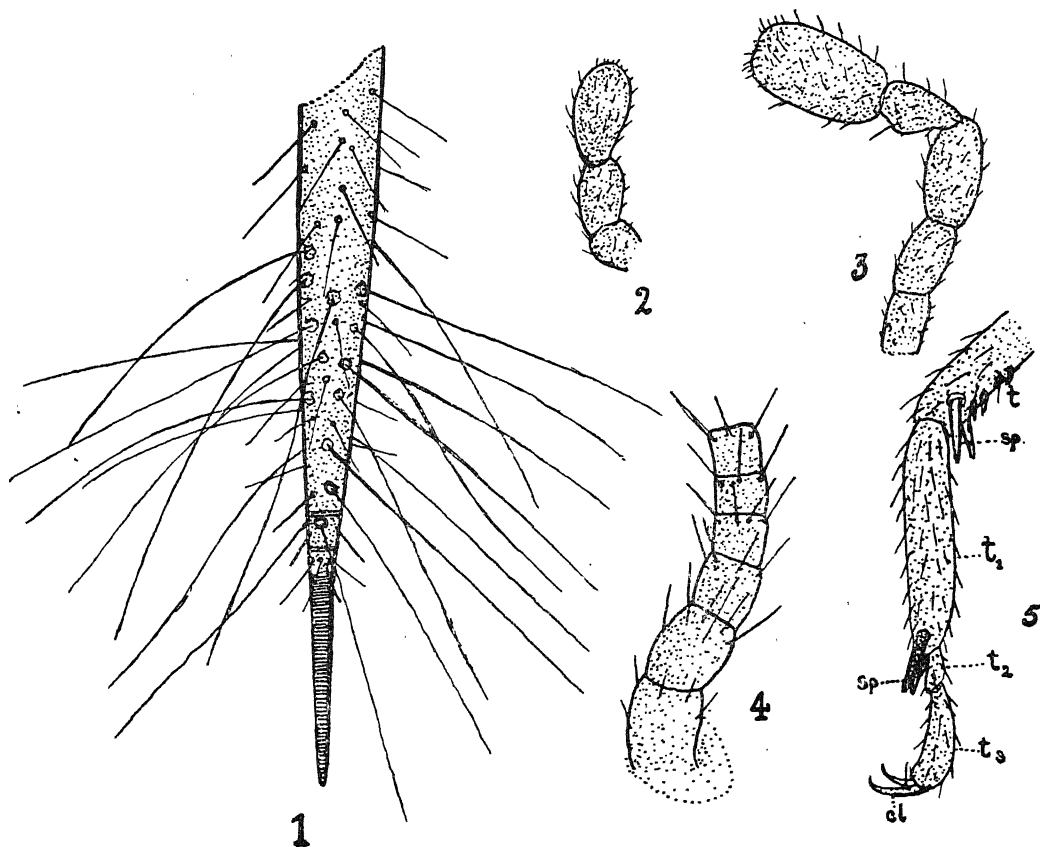
Apterous. Head and prothorax well developed. Antennae of several segments; not moniliform; segments short and cylindrical. Maxillary palpi 5-jointed. Labial palpi 3-jointed. Tarsi 3-jointed. Cerci long, tapering towards the apex; 4-jointed.

MENONIA COCHINENSIS, SPECIES NOV.

General colour yellowish-brown. Head is bent at right angles to the main axis of the body and bears a few scattered hairs. Clypeus slightly convex, resembling those of Psocids. Antennae (fig. I.4.) are broken in the specimen and the stump consists of only six segments. The lengths of these segments are in the ratio 4 : 4 : $3\frac{1}{2}$: $3\frac{1}{2}$: $2\frac{1}{2}$: 3. Maxillary palpi (fig. I.3.) 5-jointed; last segment broadly oblong, about two-thirds as broad as long. Ratio of the segments of the maxillary palpi is 3 : $3\frac{1}{2}$: 5 : $3\frac{1}{2}$: 7. Labial palpi (fig. I.2.) 3-jointed; pale yellowish-brown. Antennae and palpi with scattered hairs. Hairs slender and more numerous at the apex of the last segment of the palpus. Eyes, small, situated on the sides of the head, at the bases of the antennae. Ocelli absent.

Prothorax well developed; colour, a tint of light chocolate brown. Comparative lengths of thoracic tergites are 2 : 1 : 1. The notal sclerites not secondarily divided by sutures. Wings entirely wanting. Legs pale yellowish-brown. Hind femora broad and well developed. Tarsi 3-jointed, last segment bearing a pair of claws. Claws rather straight with pointed and curved apices. The pro-thoracic tibiae carry a spur towards their apices. The first segment of the pro-thoracic tarsi bears about nine strong spinous hairs arranged in a line on elevated chitinous outgrowths which resemble the "Ctenidia" of the meta-thoracic tarsi of certain Psocids. The meta-thoracic tibiae carry two conspicuous spines towards their apices and three short spines proximal to these arranged as shown in the figure (fig. I.5). The first tarsal segments of the meta-thoracic legs bear a pair of stout spurs at their apices. Ratio of the hind tarsal segments is 6 : 1 : 3.

Abdomen yellowish-brown. There are ten distinct tergites. The last segment bears a pair of cerci. Cerci (fig. I.1) composed of four segments. The first cercal segments are very long and broad at the base; second and third segments very short and the last



Text fig. I—*Menonia cochinensis*. Sp. nov. (×140 approx.).

1 cercus; 2 labial palpus; 3 maxillary palpus; 4 antenna; 5 posterior part of the tibia, tarsal segments and claws of the meta-thoracic leg.

t, tibia; t₁-t₃, tarsal segments; cl, claws; sp, spines.

segments about half as long as the first. The first three cercal segments carry both macrotrichia and sensory hairs. The last segment is narrow and annulated and devoid of hairs.

Measurements:—

Length of body (excluding cerci) 1·27 mm.

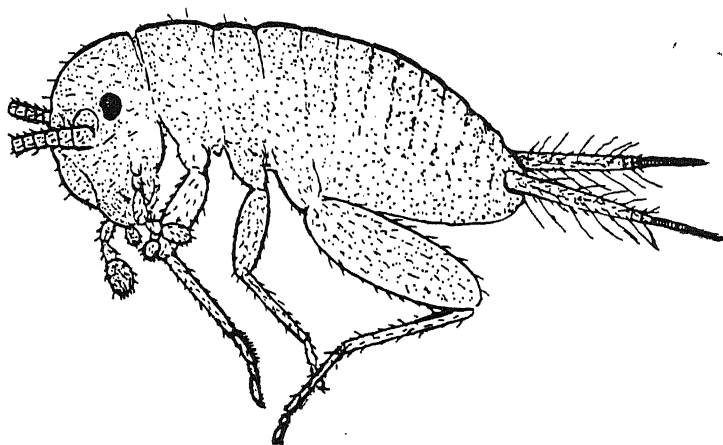
Length of cerci 0·6 mm.

Locality:—

South India. (Tripunithura—Cochin State).

Date of collection:—

15-4-1935. One specimen (♀) collected from dry foliage on the ground.



Text. fig. II—*Menonia cochinensis*, sp. nov. Lateral view of the whole animal. (Legs of one side not shown). (× 50 approx.)

The general characters, three-jointed labial palpi and the cerci, place this insect in the order Zoraptera. But it differs from species of *Zorotypus* in the possession of three-jointed tarsi and absence of moniliform antennae. Therefore I have no hesitation in creating a new genus for this insect.

I have great pleasure in naming this insect after my colleague and student M.G.R. Menon who has collected it.

NOTES ON OLIGOTOMA COLLECTED FROM BOMBAY
AND COCHIN TOGETHER WITH THE
DESCRIPTION OF A NEW SPECIES
(*With three plates.*)

BY

RAMDAS MENON & C. J. GEORGE

(Department of Biology, Wilson College)

Introduction

Species of *Oligotoma* recorded from India are few. *O.saundersi*, the first to be recorded, was described as early as 1837 by Westwood. This was followed by the descriptions of *O.latreillei* (Rambur, 1842); *O.michaeli* McLachlan, 1878; *O.ceylonica* Enderlein, 1912; *O.greeniana* Enderlein, 1912; *O.ceylonica* Enderl. var. *variegata* Mukerji, 1935 and *O.minuta* Mukerji 1935.

The Oligotomids so far collected from Bombay and Cochin consist of *O.saundersi*, *O.latreillei*, *O.ceylonica* var. *variegata*, and a species new to science which is described below as *O.asymmetrica*. Though there are a few minor differences we consider our first species is *O.saundersi* and give below a detailed description of its posterior-most segment and appendages which are of great taxonomic value. Similarly for *O.latreillei*, we take this opportunity to give a full description of the terminal segment. There are in our collection as many as eighteen specimens of *O.ceylonica* var. *variegata* and we have been able to note the extent of variation of the terminal segment of this variety.

A table of comparative measurements of the species concerned is appended.

Habits

During the monsoon months in Bombay, extending from the middle of June to the middle of September, one often comes across a number of Oligotomid webs on old walls overgrown with moss. They are easily mistaken for those of spiders, but on a closer examination each web will be found to be inhabited by a single Oligotomid. Sometimes, along with a mother, a number of young ones also may be seen under the web. During the hotter months of the year the Oligotomids are never seen inhabiting such exposed places; instead they are found to recede into crevices, under barks of trees and such other humid and shady places. This probably shows their preference to a moist atmosphere.

1. OLIGOTOMA SAUNDERSI Westwood, 1837.

(Plate I, figs. 1a & 1b).

The last abdominal segment of this species presents the following features. The tenth tergum is divided into three unequal plates. Of these the median one (m.p.) is comparatively small and its posterior margin is bluntly rounded. The right tergal plate (r.t.) is broad at the base and is produced posteriorly into a finger-shaped process (r.p.). This process is a little bulged at about the middle and is directed towards the left cercus. Its acuminate apex carries on the right a short lateral spinous process. The left tergal plate (l.t.) is circular basally and arched dorsally and it bears a bi-lobed appendage posteriorly (l.p.). The left lobe of this appendage is short and spiniform and is curved towards the inner side. This lobe is not present in some specimens. The right lobe of the left tergal process is produced into two curved and pointed teeth. The last sternite (the fused ninth and tenth sternites—s.t.) is almost triangular in shape and is directed towards the left cercus. This species is said to bear on the apex of the last sternite a pair of hooks, disposed right and left. In our specimens these hooks are however absent.

The cerci are two-jointed. The left cercus is attached to a basal piece (the vestigial eleventh segment) (l.c.b.p.) which is narrow and elongated. This is bi-lobed in some specimens; the right lobe is bluntly rounded and the left one is produced into a spur-like process which is either free or attached to the basal segment of the left cercus. This process is unrepresented in some specimens. The basal segment of the left cercus (l.c.₁) is club-shaped and its inner margin is fused along the whole length of the basal piece. The basal segment of the right cercus (r.c.₁) is somewhat conical in shape and is slightly shorter than the basal segment of the left cercus. The terminal cercal segments (l.c.₂ and r.c.₂) are sub-equal and elongate-oval in shape.

Locality and date of collection :—Mahim, (Bombay City), 8. vii. 1934, 1 (♂); Thana, (Salsette), 15. vii. 1934, 1 (♂); Santa Cruz, (Salsette), 24. xi. 1935, 3 (♂); Ernakulam, (Cochin State), 30. xii. 1935, 1 (♂). All at light. Collected by Ramdas Menon.

2. OLIGOTOMA LATREILLEI Rambur, 1842.

(Plate I, figs. 2a & 2b.).

The tenth tergum presents the following features. It is divided into three plates. The middle plate (m.p.) is almost

triangular in shape and rounded at the apex. The right tergal plate (r.t.) is broad at the base and is narrowed posteriorly into a finger-shaped process (r.p.). This process is slightly swollen at the tip and is directed towards the left cercus. The left tergal plate (l.t.) is semicircular at the base and is posteriorly produced into a narrow finger-shaped process (l.p.). This process is rather pointed and extends to about two-thirds the length of the right tergal process and ends between the two lobes of the last sternite (s.t.). The anterior half of this sternal plate is comparatively broad and its posterior half is almost boat-shaped. Its apex is bi-lobed and the lobes are separated by a concave, strongly chitinated posterior margin. The right lobe of this is stout, turned dorsad and bears at the apex a cup-shaped depression. The left lobe is short and bluntly pointed.

The cerci are two-jointed and somewhat asymmetrical. The left cercus is attached to a basal piece (l. c. b. p.) which is posteriorly elongated. The basal segment of the left cercus (l.c.₁) is club-shaped and attached along the whole length of the outer margin of the basal piece. The basal segment of the right cercus (r.c.₁) is broader at the base than at the apex and is somewhat shorter than the basal segment of the left cercus. The terminal cercal segments (l. c.₂ & r. c.₂) are sub-equal and elongate-oval.

Locality and date of collection:—Santa Cruz, (Salsette), 25. viii. 1935, 3 (♂), 26. viii. 1935, 1 (♂), and 24. xi. 1935, 1 (♂); Ernakulam, (Cochin State), 30. xii. 1935, 8 (♂). All at light. Collected by Ramdas Menon.

3. OLIGOTOMA CEYLONICA Enderl. var VARIEGATA Mukerji 1935.* (Plate II).

In the general organisation of the terminal segment and appendages all specimens of this species in our collection agree with *O.ceylonica* var. *variegata*; but in certain features some differences are to be noticed.

The tip of the right tergal process usually ends in two protuberances separated by a concavity as described by Mukerji; but the sizes of these protuberances are found to vary to a greater extent than shown by him. In some specimens this process ends in a bluntly rounded tip. The tip of the left process may reach or protrude beyond the limit of the last sternite (s.t., fig. 2a), but in Mukerji's specimens it appears in every case to extend beyond

*Mukerji in Rec. Ind. Museum. Vol. XXXVII Part I, 1935, pp. 4-7, text fig. 2.

the sternite. The posterior margin of the last sternite is rounded in Mukerji's specimens; but in our specimens it is either rounded or bluntly acute as shown in the figure.

The cavity on the basal segment of the left cercus in our specimens exhibits a wider range of variation than shown by Mukerji (Fig. 1. A-F). In some specimens the posterior outer margin of this cavity is even produced into a stout blunt spine.

The specimens in our collection vary in length, measuring from 5 m.m. to 7 m.m., excluding cerci. Mukerji's specimens appear to be smaller in size, measuring only 5.5 mm.

In this connection we also wish to mention that Needham's figure* of *E. michaeli* resembles some of our specimens which show the extremely well developed cavity on the left cercus. Therefore we are tempted to conclude that he might have had before him a specimen of *Oligotoma ceylonica* var. *variegata*.

Locality and date of collection:— Santa Cruz, (Salsette), 10-vi-1935, 1 (♂), at light; 16-vi-1935, 2 (♂), under web on old moss-grown walls; 17-xi-1935, 1 (♂), at light; 23-xi-1935, 1 (♂), at light; 25-xi-1935, 1 (♂), at light; Ernakulam, (Cochin State), 28-ix-1935, 2 (♂), at light; 30-xii-1935, 10 (♂), at light. Collected by Ramdas Menon.

4. OLIGOTOMA ASYMMETRICA, Spec. nov. (Plate III).

General colour brownish-black. Head, antennae and prothorax almost black; Meso- and meta-thorax, legs and abdomen somewhat lighter; wings greyish-black; veins almost brownish black; "pseudo-radial lines" brownish; hyaline bands narrow and well marked out.

Head almost roundish. Eyes reniform, slightly bulging out laterally, about two-thirds visible from above; deep black. Antennae (fig. 3) 23-jointed; segments cylindrical and densely pubescent. First six antennal segments are in the ratio 12 : 6 : 10 : 11 : 13 : 13. Maxillary palpi (fig. 2) 5-jointed; segments in the ratio 5 : 5 : 6 : 9 : 12.

Thoracic segments well-developed. Pro-thorax with a deep transverse and shallow longitudinal sulcus; rectangular; somewhat longer than broad. Meso- and meta-thorax almost of the same type of construction. Each of these bears on the dorsal side a shallow depression extending over the anterior half of the prescutum. The meso-notum bears a posterior semicircular scutellar area.

*Needham in Rec. Ind. Museum, Vol. III 1909, Plate xx.

Wings (fig. 4) are long and narrow as in other Embiids. They reach to about the tip of the last abdominal tergite. The following veins are distinctly discernible; the basal part of sc., r_1 , r_{2+3} , base of r_{4+5} , cu and a. and the radial cross-veins. All the other veins are very indistinctly demarcated. The radial cross-veins are about four in number in both wings. Macro- and micro-trichia are present on the margins, veins and membrane.

The abdomen is ten segmented. The first abdominal segment is fused with the meta-thorax. Segments 2-8 are sub-equal in size. Ninth segment is slightly compressed. The tenth tergum (Fig. 1) is divided into three plates. The middle plate (m.p.), is triangular in shape and rounded at the apex. The right tergal plate (r.t.) is broad at the base and is posteriorly produced into a finger-shaped process (r.p.). This process slowly narrows down into a bifid apex, as shown in the figure. The left plate (l.t.) is also broad at the base and its posterior margin is produced into two lobes. Of these the inner one (i.l.t.) is bluntly rounded; the outer one is produced into a long finger-shaped process (o.l.t.). The last abdominal sternite is almost triangular in shape; its apex is slightly swollen and bent towards the dorsal side and in the concavity formed by this bend rests the tip of the left tergal process.

The cerci (Fig. 1) are two-jointed and exhibit a more pronounced asymmetry. The left cercus is attached to a basal piece (l.c.b.p.). This piece is short and cylindrical and resembles that of *O. ceylonica* var. *variegata*. The basal segment of the left cercus is irregularly flattened out and twisted in a peculiar way as shown in the figure (l.c.₁). The basal segment of the right cercus (r.c.₁) is almost cylindrical in shape. The terminal cercal segments sub-equal and elongate oval.

Locality and date of collection:—Santa Cruz, (Salsette), 14-viii-1935, 1 (♂), at light. Collected by Ramdas Menon.

Acknowledgment

We take this opportunity to express our gratitude to the authorities of the Royal Institute of Science, Bombay, and the Imperial Institute of Agricultural Research, Pusa, for the loan of the necessary books from their libraries.

Literature

A list of literature on the Order is given by Okajima, (Jour. Coll. Agr., Imp. Univers., Tokyo, Vol. VII, 1919-1926) and Mukerji (Rec. Ind. Mus. Vol. XXIX. P. IV, 1927) and we deem it unnecessary to repeat it here.

Explanation of the Plates

- Plate I. Fig. 1a. *Oligotoma saundersi* Westwood. Terminal segment and appendages. Dorsal view. ($\times 50$ approx.).
- Fig. 1b. *Oligotoma saundersi* Westwood. Last sternite and the parts associated with it. Ventral view. ($\times 50$ approx.).
- Fig. 2a. *Oligotoma latreillei* (Rambur). Terminal segment and appendages. Dorsal view. ($\times 50$ approx.).
- Fig. 2b. *Oligotoma latreillei* (Rambur). Last sternite. Ventral view. ($\times 85$ approx.).
- Plate II. Fig. 1.A-F. *Oligotoma ceylonica* var. *variegata* Mukerji. The basal segments of the left cercus showing the extent of variation of the concavity. A-C. Cochin forms. D-F. Bombay forms. ($\times 105$ approx.).
- Fig. 2a. *Oligotoma ceylonica* var. *variegata* Mukerji. The terminal segment and appendages. Dorsal view ($\times 85$ approx.).
- Fig. 2b. *Oligotoma ceylonica* var. *variegata* Mukerji. The last sternite and the parts associated with it. Ventral view. ($\times 85$ approx.).
- Plate III. Fig. 1. *Oligotoma asymmetrica*, sp. nov. Terminal segment and appendages, Dorsal view, ($\times 50$ approx.).
- Fig. 2. *Oligotoma asymmetrica*, sp. nov. Maxillary palp. ($\times 50$ approx.).
- Fig. 3. *Oligotoma asymmetrica*, sp. nov. Antenna. (First 8 segments.) ($\times 35$ approx.).
- Fig. 4. *Oligotoma asymmetrica*, sp. nov. Right pair of wings. ($\times 18$ approx.).

Lettering

- i.l.t. = inner lobe of left tergite.
 l.c.₁ = basal segment of left cercus.
 l.c.₂ = terminal segment of left cercus.
 l.c.b.p. = basal piece of left cercus.
 l.p. = process of left tergite.
 l.t. = left tergal plate.
 m.p. = median tergal plate.
 o.l.t. = outer lobe of left tergite.
 r.c.₁ = basal segment of right cercus.
 r.c.₂ = terminal segment of right cercus.
 r.p. = process of right tergite.
 r.t. = right tergal plate.
 st. = last sternite.

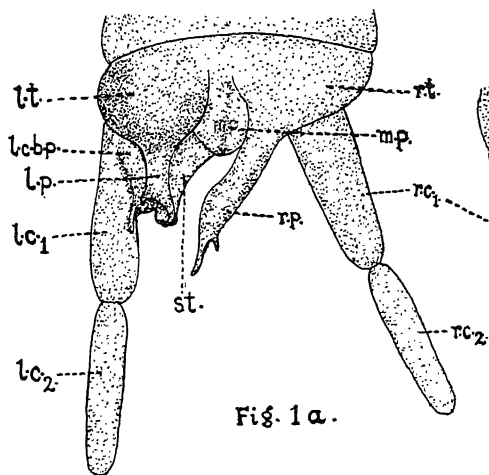


Fig. 1a.

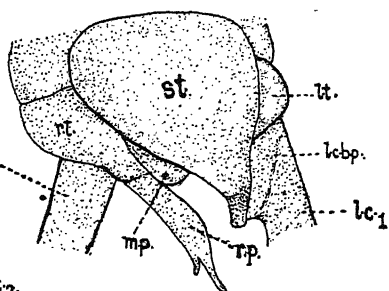


Fig. 1b.

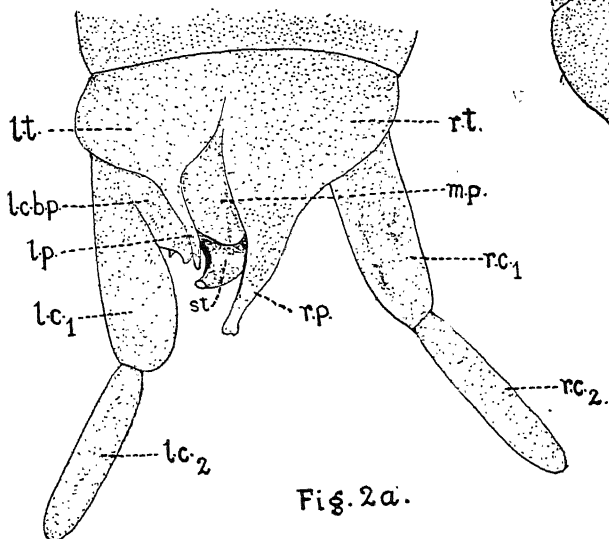


Fig. 2a.

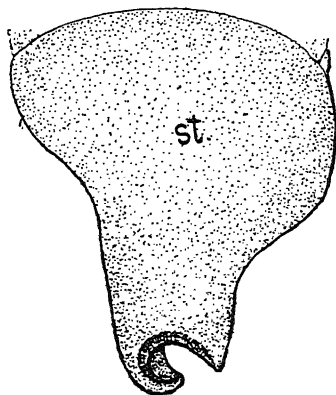


Fig. 2b.

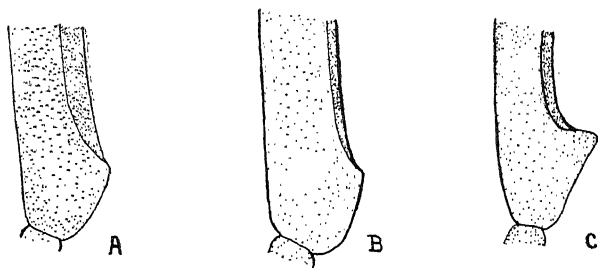


Fig. 1.

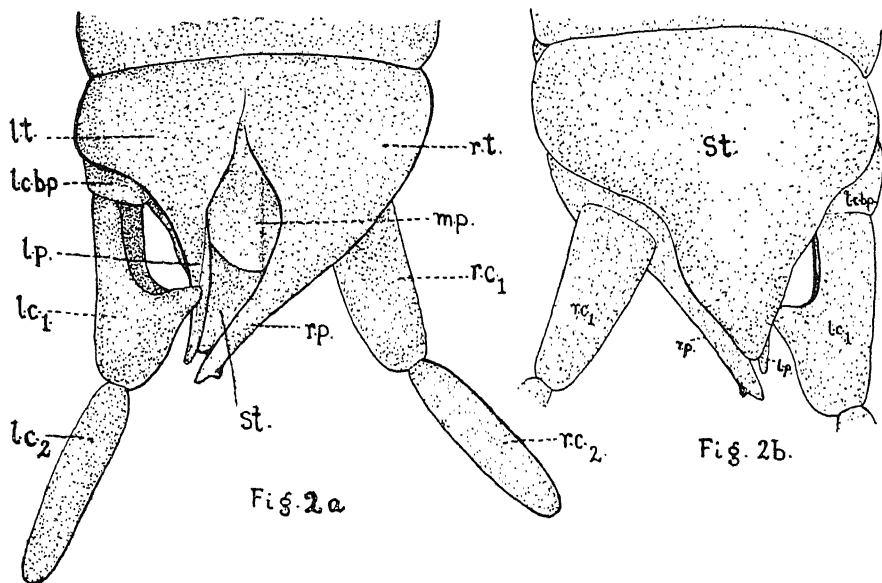
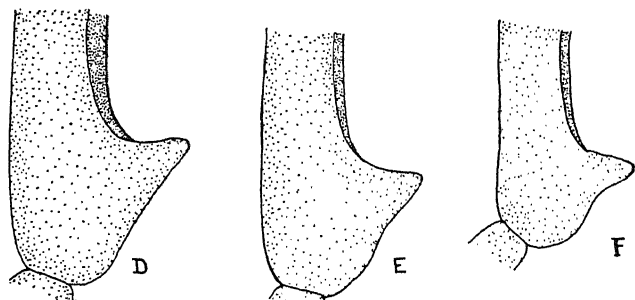
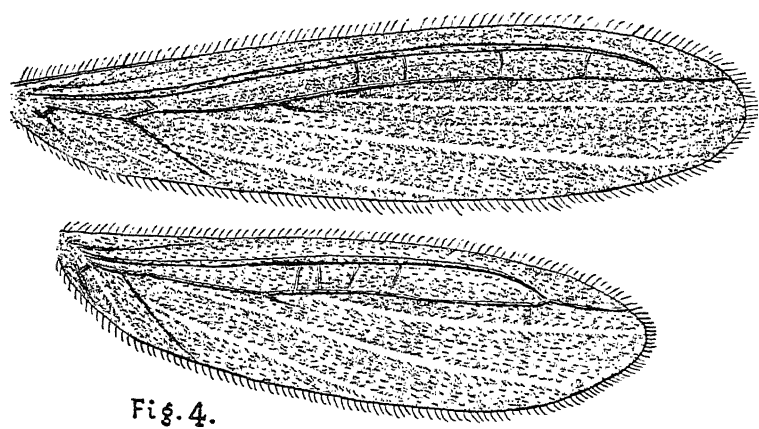
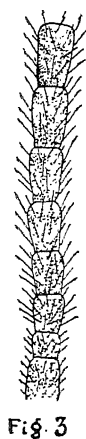
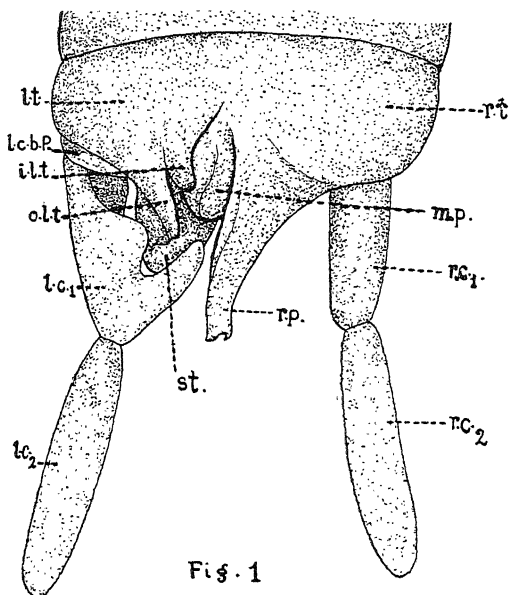


Fig. 2b.



Appendix

Comparative measurements of the species of *Oligotoma* collected from Bombay and Cochin :—

| | <i>O.saundersi.</i> | <i>O.latreillei.</i> | <i>O.ceylonica</i> var. <i>variegata.</i> | <i>O.asymmetrica.</i> |
|--|---------------------|----------------------|---|-----------------------|
| Length of body. | 7·7—8mm. | 8·6mm. | 6—7mm. | 9·3mm. |
| Length of head. | 1·14mm. | 1·23mm. | ·97—1·14mm. | 1·54mm. |
| Breadth of head. | ·97mm | ·91mm. | ·69—1·03mm. | 1·2mm. |
| No. of antennal joints. | 18 | 19 | 16 | 23 |
| Length of Prothorax. | ·51mm. | ·63mm. | ·46—·51mm. | ·85mm. |
| Breadth of Prothorax. | ·54mm. | ·57mm. | ·51—·57mm. | ·74mm. |
| Length of mesothorax. | 1·08mm. | 1·14mm. | ·97—1·03mm. | 1·4mm. |
| Breadth of mesothorax. | ·97mm. | 1·09mm. | ·86mm. | 1·3mm. |
| Length of metathorax (including 1st. abd. segment) | 1·08mm. | 1·03mm. | ·91—1·03mm | 1·3mm. |
| Breadth of metathorax. | ·85mm. | 1·03mm. | ·74—·86mm. | ·98mm. |
| Length of forewing. | 5·8—6mm. | 5·7mm. | 4·6—5·03mm. | 5·5mm. |
| Breadth of forewing. | 4·9mm. | 4·9mm. | 3·7—4·17mm. | 4·5mm. |

PROBOSCIS OF THALASSEMA BOMBAYENSIS

(PRASHAD AND AWATI)

(With 8 text-figures)

BY

P. R. AWATI

(Department of Zoology, Royal Institute of Science, Bombay)

The proboscis is a characteristic structure found amongst all the Echiuroids. It is a prolongation of the dorsal lip or the preoral part of the larva as Lacaze-Duthier and Spengel (3) have made out. This dorsal lip projects more or less over the mouth as in other annelida. It is a fleshy and at the same time highly contractile organ which when fully extended, assumes an almost ribbon-like form in some and spade-like in others. In the normal condition, however, it is more or less cylindrical, the dorsal surface being fleshy and convex in outline, while the ventral surface is almost flat, its margins being rolled in. This flat surface bears longitudinal folds which form channels on its surface. The margins of the proboscis are wavy and crenulated and a little rolled while the tip is subtruncate and assumes roughly a semi-circular shape. Its basal portion is very much narrower than its mid region and the margins in this region (basal) are stiff and strongly incurved. They form the sides of a sort of a funnel through which the water flows into the mouth which is situated at the base of that funnel.

The sides of the proboscis can be curved in to such an extent so as to form almost a narrow and deep gutter (channel), its bottom being formed by its ventral median surface.

The proboscis is a more or less stoutly built structure having a spongy mass of a connective tissue containing muscles, circumpharyngeal commissures of the nerve cord, dorsal and marginal blood vessels and lastly narrow coelomic marginal sinuses enclosing the latter (Fig. 1).

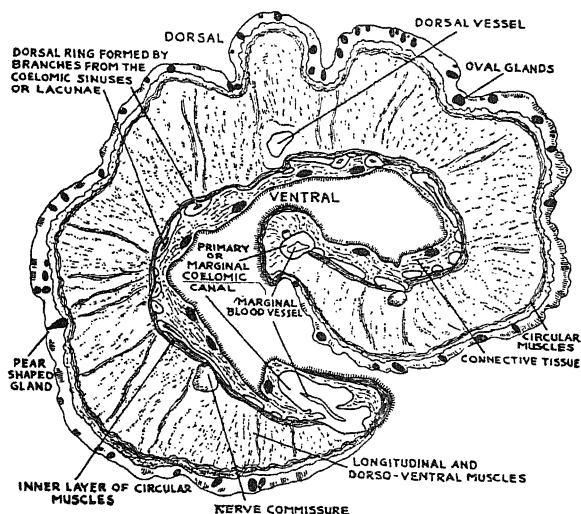
The tissues forming the proboscis are:—(Figs. 1, 2 and 3).

(1) The Cuticle. It covers the entire dorsal epidermal layer and is almost similar to that of the trunk. It is absent on the ventral surface. It is rather a thick non-cellular structure (Fig. 2).

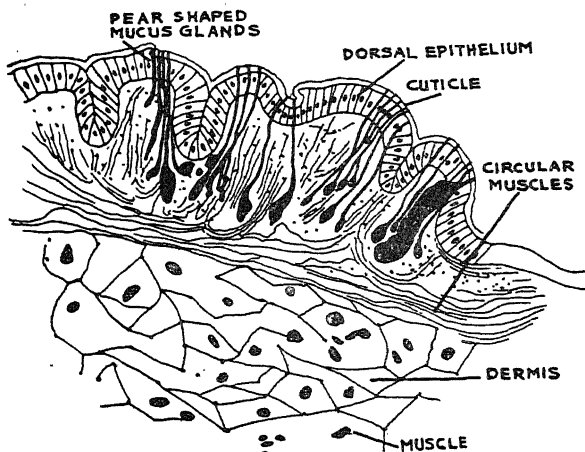
(2) The Epidermis. The epidermal linings of the dorsal and the ventral surfaces are different. The dorsal epithelium, like that of the trunk consists of cylindrical and non-ciliated cells amongst

which are found embedded ducts of gland cells as well as external parts of receptors (Fig. 2).

The ventral epithelium of the proboscis lining the gutter and the margins consists of short cylindrical ciliated cells, each with a nucleus in the centre. There are also glandular cells and ducts of



Text fig. 1.—Transverse section of the proboscis, $\times 40$.

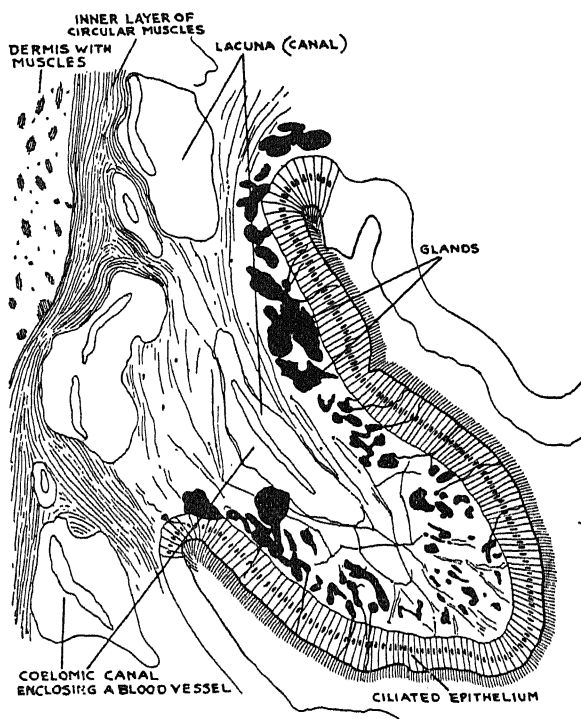


Text fig. 2.—Dorsal surface of the proboscis, $\times 200$.

other glands in between these cells. These two surfaces of the proboscis, dorsal and ventral, have two different functions to perform; the dorsal surface is muscular and tactile while the ventral

forms the gutter to transport water and food into the mouth of the animal (Fig. 3).

(3) The Dermis. It is the principal tissue which forms the core of the proboscis. It forms the dense ground substance, in which are found connective tissue cells and fibres and muscles fibres forming a close network. The connective tissue between the inner layer of the circular muscles and the ventral epithelium is on the other hand loosely arranged. There are sinuses formed by the network of the coelomic canals crossing and re-crossing each other (Figs. 3 and 6). In the dermis are found bands of muscles which are smooth. These muscles are differently arranged :



Text Fig. 3—Ventral surface of the proboscis, $\times 200$.

(i) Circular muscles. There are two thin layers of the circular muscles; one immediately beneath the dorsal epidermis and outside the hypodermal connective tissue, while the other layer encircles the ventral surface between the dermis and the chain of the sinuses (lacunae). Contractions of these muscles, helped by the turgescence of the canals by inrushing of the body fluid, tend to lengthen the proboscis,

(ii) Longitudinal muscles. The bundles of longitudinal muscles are continuous with those of the trunk and are found mostly on the dorsal side. The contractions of these muscles tend to shorten the proboscis.

(iii) Oblique muscles. The oblique muscles form a part of the circular muscles. They run along the margins of the proboscis. Contractions and relaxations of these muscles change the form and the length of the gutter and the margins.

(iv) Dorso-Ventral muscles. These dorso-ventral muscles run from the dorsal to the ventral surface through the dermis. The contractions of these muscles tend to flatten the proboscis and make it more or less spade-like with the broad tip.

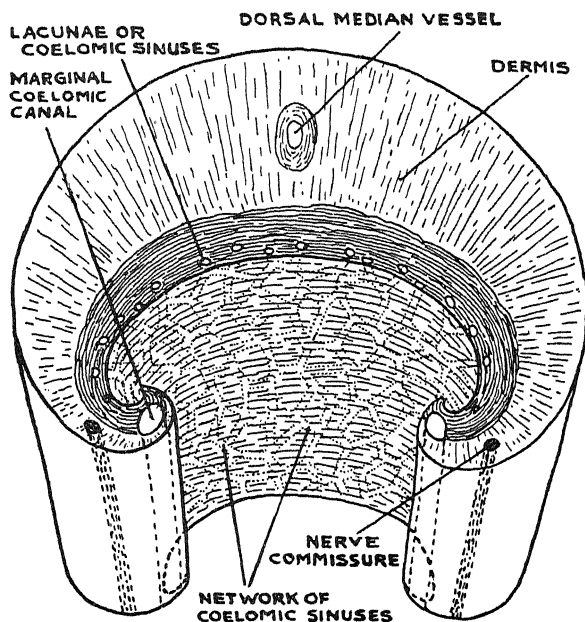
(4) Glandular tissue. It is found between the dorsal epithelium and the outer layer of the circular muscles. It consists of groups of individual gland cells. Some of these are more or less pear-shaped, having a long neck and a longer duct which passes through the epithelial layer and pierces through the cuticle to open on the dorsal surface, while others are more or less oval. (Figs. 1 and 2).

The glandular tissue on the ventral side on the other hand which is found in a loose connective tissue, consists of irregularly shaped gland cells with or without necks. The ducts are extremely thin and narrow. They open on the ventral surface after passing through the ciliated epithelium (Fig. 3).

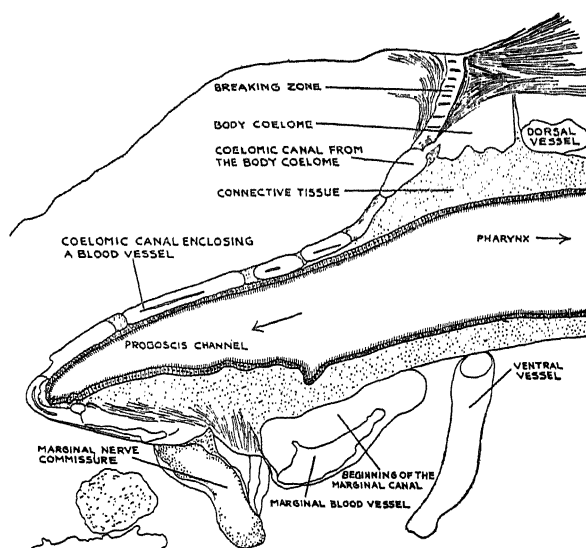
(5) Coelomic canals (Lacunae). In a transverse section a series of isolated canals or lacunae are seen forming a chain along the ventral surface (Figs. 1 and 4). They are found lying between the inner layer of the circular muscles and the loose connective tissue lying underneath. Each sinus is seen enclosing a vacuole which is nothing but a part of a blood vessel. The marginal sinuses (canals) are bigger than the rest.

The smaller sinuses are the cut ends of the coelomic canals which form a network in the loose connective tissue and also open into each other at the crossing points. These canals are branched off as secondary canals from the two big ones found along each margin of the proboscis. The latter (marginal canals) are the primary canals which are the direct continuations from the body coelome and are found running along the margin between the latter and nerve commissure on each side. These primary coelomic canals can be traced to the main body coelome in a series of transverse sections (Fig. 5). The presence of the network of the canals and inter-communications among them can be easily demonstrated. A coloured fluid when injected through any of the

sinuses, comes out through all other sinuses—big and small. The fluid while passing through the network of these canals leaves

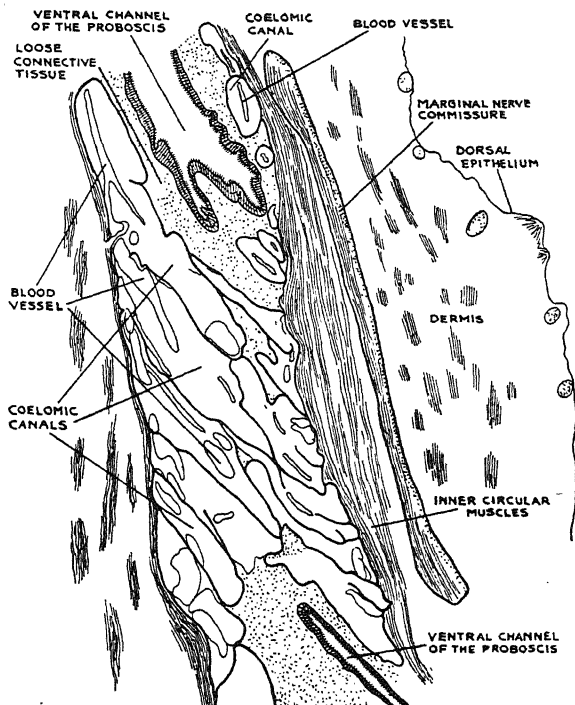


Text fig. 4—Showing diagrammatically a network of coelomic canals just beneath the ventral epithelium of the proboscis.



Text fig. 5—Median longitudinal section of the proboscis showing the origin of the marginal coelomic canals in the proboscis, $\times 40$.

its stain behind. By clearing the portion injected, a network can be made out (Fig. 4). An oblique sagittal section of the proboscis reveals the presence of this network (Fig. 6).



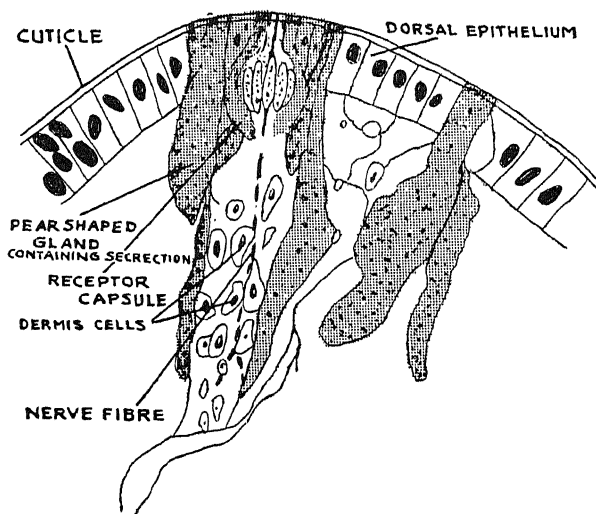
Text fig. 6—Oblique horizontal section of the proboscis showing the network of the coelomic canals, $\times 40$.

(6) Blood vessels. There are three main blood-vessels in the proboscis. One of them is the dorsal vessel which runs from the base to the tip of the proboscis almost through the centre of the dermis, while the other two form marginal vessels running parallel with the margins of the proboscis. All the blood-vessels give out branches which run through the tissue of the proboscis. The marginal vessels and their branches are, however, enclosed in the coelomic canals. These latter blood vessels can be differentiated from the coelomic canals by the fact that the former are rather well lined with the endothelium while the latter have a peritoneal lining and sometimes sexual cells and coelomic corpuscles are found in them.

The dorsal blood vessel is on the other hand, quite different in appearance from the marginal vessels. In a transverse section it

shows the endothelial lining and a thick layer of fibres. On the outside of the fibrous layer there is a thick covering of a dense non-cellular tissue. Along its course it sends out branches into the dermis.

(7) MARGINAL NERVE COMMISSURES (Figs. 1 and 6). There are two circum-pharyngeal commissures running along both the margins of the proboscis. Nerve branches are given off from these commissures which form a network in the dermis.

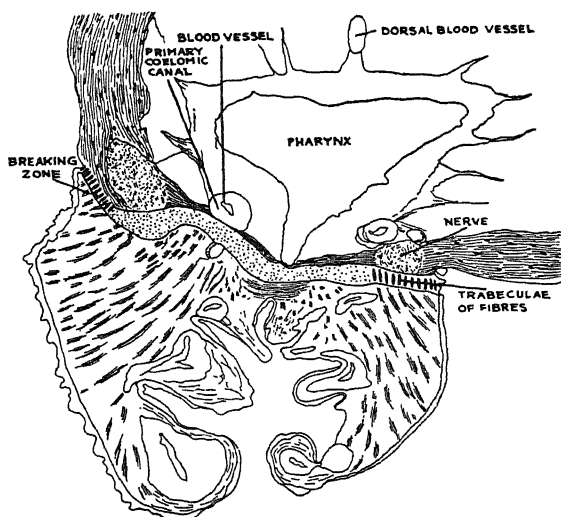


Text fig. 7—Showing a receptor capsule and pear-shaped glands on the dorsal surface of the proboscis, $\times 900$.

(8) CAPSULES OF RECEPTORS (Fig. 7). They are found in the dorsal epithelium, embedded partly in the dermis and partly in the epithelium. Each capsule is generally located in between many pear-shaped glands. It consists of the central neuro-epithelial cell having a short process at the outer end and longer and thinner one at the inner. The short process is the sensory hair which projects a little outside the dorsal surface. The longer process joins on to a small delicate nerve fibre which is given from one of the commissures. The side cells two or more on each side are the supporting cells. The whole structure is enclosed in the modified dermal tissue.

No receptor capsules are found on the ventral surface. Their absence may be due to the fact that the whole of the ventral surface is sensory.

BREAKING ZONE BETWEEN THE PROBOSCIS AND THE TRUNK OF THE BODY (Figs. 6 and 8). The proboscis can be easily detached or broken off from the trunk at the slightest irritation. In order to facilitate such an easy detachment, a zone is formed between the trunk and the proboscis, consisting of thin trabeculae of the connective and muscular tissue, the fibres of which bridge over the vacuolated space. These fibres snap asunder when the trunk and the proboscis are being contracted at the same time but in opposite directions. The proboscis falls off and the vacuolated space where the breaking zone is formed contracts and closes up. The fluid from the body-cavity is thus prevented from oozing to the outside by such a closing mechanism.



Text fig. 8—Showing the breaking zone of the proboscis, $\times 40$.

Functions of the proboscis. Some of the important functions which can be ascribed to this organ of *Thalassema* are :—

(i) **Transportation of food and water.** By forming a gutter on the ventral surface and by producing currents by ciliary movements of the ventral epithelium, water containing small organisms and sand particles is made to flow along the ventral surface into the mouth. In the secretion of the glands found along the ventral surface are caught small organisms, and particles of sand which are then carried into the alimentary canal with the water.

(ii) **Burrowing organ.** The coelomic spaces in the proboscis become turgid when filled with the coelomic fluid thus making the proboscis rigid for burrowing purposes into the soft sand or clay.

This turgid and hence rigid proboscis can be compared with the foot of a burrowing bivalve in which the turgidity of the organ is, however, due to the influx of the blood into it.

(iii) Respiration. The coelomic fluid contained in the coelomic canals of the proboscis performs a respiratory function. These canals line the inside of the ventral surface along which a continuous stream of fresh water is passing. Owing to a very thin partition between the coelomic fluid on one hand and water on the other, the former is thus able to give up its carbon dioxide into and take in oxygen from the latter. Besides oxygenation of the coelomic fluid, the blood contained in blood vessels is also oxygenated.

(iv) Besides discharging these important functions, the proboscis may act as an organ of touch and taste because of the presence of receptor capsules and sensory ventral epithelium.

(v) On account of its adhesiveness owing to secretion of the glands on the ventral surface, the proboscis may enable the animal to creep slowly. It has been seen in smaller specimens under observation that the ventral surface of the proboscis when completely flat, firmly adheres to the surface of the substratum. It then contracts and drags the animal slowly after it.

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COMMON SAGITTAE OF THE BOMBAY HARBOUR
(*With 3 Text and 3 Plate figures.*)

BY

S. H. LELE & (MISS) P. B. GAE

(Department of Zoology, Royal Institute of Science, Bombay)

The present paper on the common sagittae of the Bombay Harbour is the second of the series of our papers on the common planktonic organisms of the Bombay Harbour being published in this journal. It is based on the plankton collected by us regularly at short intervals from October 1932 to February 1934 and at long intervals since then. These arrow-worms are usually found throughout the year and although colourless and transparent they attract one's notice by their darting movements.

All the arrow-worms found in the Bombay Harbour belong to the genus sagitta which is oceanic and has a world-wide distribution. It consists of about 30 species which have been "cursorily" described and include "a number of very similar forms" according to Fowler (2). We have therefore examined numerous local specimens and based on this investigation we have given here the characters of these species.

SAGITTA GARDINERI

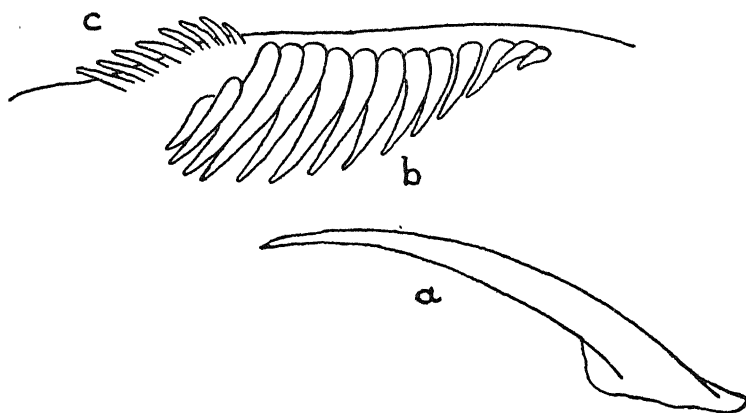
L. Doncaster. Chaetognatha: Fauna and Geography of the Maldiva and Laccadive Archipelagoes, Vol. 1, p. 212, 1902.

CHARACTERS :—The body (Plate 1, Fig. 1) is spindle-shaped, transparent and thin-walled. In living and well-preserved specimens it is tumid, otherwise flaccid or contracted and wrinkled. The head is broad and short but appears rather small in contraction. There is a distinct neck without a collarette. The trunk is thickest in front of its middle. It tapers rapidly forward and gradually backward. The tail including the caudal fin is nearly one-fifth of the total length of the body, including the caudal fin, i.e. from the tip of the head to the tip of the caudal fin. It is marked off from the trunk by a slight constriction. The total length of the body varies from 5 mm. to 23 mm.

The anterior fins are narrow and short, beginning anteriorly behind the middle of the trunk. Their widest part is behind their middle. The posterior fins situated some distance behind the

anterior fins are equally short but broader. Their widest part is about the level of the tail-septum and they are situated more in its front than behind. The fin rays of the paired fins do not extend quite to the base. The caudal fin is large and rounded.

The 8 to 10 prehensile spines are slender and slightly curved (Text Fig. 1). The anterior set of teeth consists of 7 or 8 short and pointed teeth slightly projecting beyond the anterior edge of the head in the middle. The posterior set bends obliquely backward and consists of 9 to 16 similar teeth of which the middle ones are long.



Text fig. 1—Armature of *S. gardineri* 18 m.m. long.
a, prehensile spine; b, posterior teeth; c, anterior teeth.

The corona ciliata is not usually found even in living and freshly preserved specimens after staining with one per cent. methyl blue solution. Out of 50 specimens carefully examined only in 4 specimens it was partially seen and in one alone it was like what has been figured by Fowler. It was situated entirely on the head just behind the cerebral ganglion and resembled an hour-glass with the top knocked off. Even after staining no tactile bodies were discovered on any part of the body. The ventral ganglion is in front of the anterior fin at a distance of the length of the latter.

The intestine is a straight and laterally compressed tube which being less contractile than the bodywall appears slightly bent sideways in preserved specimens. The ovaries are usually short and stout and often curved outward at the tip. In a few large specimens they were found to extend beyond the posterior fins. In mature specimens the chambers in the tail segment are found to be full of sperm morulae. The latter are seen moving round, continuously inside them. The seminal vesicles are spherical and

close to the caudal fins. The distance between the genital openings was found to vary between ten and twelve per cent. of the total length of the body.

FORMULA OF *S. GARDINERI*

| Total Length of the body in mm. | Percentage of distance between genital openings in total length. | Prehensile spines. | Anterior teeth. | Posterior teeth. |
|---------------------------------|--|--------------------|-----------------|------------------|
| 4.5 | 12 | 9 | 7 | 9 |
| 11 | 11 | 9 | 8 | 12 |
| 14.5 | 10.5 | 10 | 7 and 8 | 14 |
| 18 | 11 | 10 | 8 | 14 |
| 21 | 12 | 9 | 8 | 16 |

REMARKS: This species was abundantly found in winter. Although it was not found in the months of March, April, and May of 1933 later collections have shown that it is not altogether absent during these months. The drawing with the camera lucida of a specimen of this species (Plate 1, Fig. 1) shows also a small trematode inside the body-cavity in front of the ovaries. Such parasitic trematodes are occasionally found wriggling inside the specimens of this as well as other species.

Sagitta enflata and *S. hexaptera* are superficially similar to this species and have been recorded at some places on the West and East Coasts of India. *S. enflata* appears to be easily separable from this species by its shorter anterior fins and the considerably longer distance between its ventral ganglion and anterior fins, as seen by John (4). The ratio of this distance to the total length of the body has been observed by him to be twice or thrice that in *S. gardineri*. In this connection it may be pointed out that Fowler's camera lucida figure of *S. enflata* agrees with that of John's *S. gardineri* on this point and also in the matter of the percentage of the distance between the genital openings in the total length. In the absence of the original specimens for comparison it may be suggested that *S. gardineri* of Doncaster is really synonymous with *S. enflata* of Grassi as previously shown by Fowler and that *S. enflata* recorded by John at Madras is a different species. *S. hexaptera* can be readily distinguished by its few anterior and posterior teeth.

SAGITTA BEDOTI

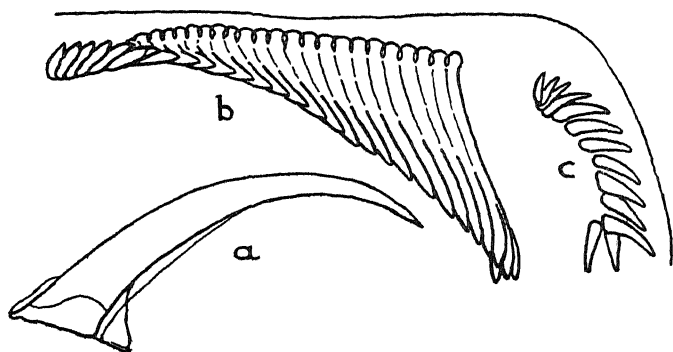
Ed. Béranek. Les Chetognathes de la Baie d'Amboine.
Revue Suisse de Zoologie. Tom. 111, p. 147, 1895.

CHARACTERS: The animal (Plate 1, Fig. 2) is like a short and

stout needle. The head is rather small and looks to the naked eye as an opaque end of the body in preserved specimens. Under a dissecting lens it is seen to be separated from the trunk by its slight dilatation. The end of the trunk behind it has a short but slight thickened epidermis which represents its collarette and makes this part of the trunk its neck. The trunk is firm and columnar with a slight bulge in the middle. In preserved specimens its sides often sink in and the trunk appears much narrow and the head more pronounced. The tail is about 30 per cent. of the total length and marked off from the trunk by a slight constriction. The total length of the animal varies between 5 mm. and 24 mm.

The anterior fins are long and wide posteriorly. They begin at the level of the ventral ganglion and gradually increase in width posteriorly. The fin rays start from the base. The posterior fins are broader than the anterior and lie more along the tail than along the trunk. Their widest part is quite behind the tail septum and they nearly reach the seminal vesicles. The distance between the anterior and the posterior fins is short but distinct. The caudal fin is roughly triangular.

There are 7 or 8 thick and strongly curved prehensile spines (Text Fig. 2). The anterior teeth vary from 10 to 13 and form a longitudinal row bending round the anterior edge of the head.



Text fig. 2—Armature of *S. bedoti* 23 mm. long.
a, prehensile spine; b, anterior teeth; c, posterior teeth.

The posterior teeth are numerous, brown and close set. Their number varies from 19 to 33. This set of teeth is more or less transverse with its one end curving backward dorsally and the other ventrally.

The corona ciliata is long, narrow and slightly sinuous. It begins in front of the eyes and extends behind for two-thirds of the

distance between the head and the ventral ganglion. Under the low power of the microscope the thin collarette is seen to be produced behind to the anterior fins in the form of a very thin but distinct epidermal lining. It becomes again visible in the interval between the anterior and the posterior fins. All over the trunk many transverse rows of tactile organs are seen. They appear as oval or circular deep blue spots when stained with methyl blue. Some tactile bodies are found on the caudal fin. Their sensory hairs appear to be stiff and straight. The ventral ganglion is small and situated one-fifth of the total length behind the anterior end.

The intestine often appears brown and baggy in preserved specimens. The ovaries are long and slender and were found to extend in some specimens beyond the posterior two-fifths of the length of the trunk. The ova inside are large and rounded and may make the ovary look septate. The female genital opening is situated on a conical papilla which stands out laterally. The testes contain sperm morulae which move round a longitudinal septum in each chamber. The seminal vesicles when tumid are spout-shaped and extend from the caudal to the posterior fin. Their external openings are situated anteriorly and directed outward. The distance between the genital openings was found to vary between 11 and 13 per cent.

FORMULA FOR *S. BEDOTI*

| Total Length in mm. | Percentage of distance bet. genital open- ings in total L. | Prehensile spines. | Anterior teeth. | Posterior teeth. |
|------------------------|---|-----------------------|--------------------|---------------------|
| 23 | ... | 8 | 13 | 29 |
| 15 | 11 | 8 | 13 | 30 |
| 13 | 11 | 8 | 11 | 26 |
| 4.7 | 13 | 8 | 13 | 19 |

REMARKS: This is the most common sagitta of Bombay and is found in fair numbers throughout the year. The length of usually found larger specimens varies between 10 mm. and 16 mm.

This species was created by Béraneck for preserved specimens from Amboina in which he could not see the corona ciliata. Later Doncaster provisionally created a new species viz. *S. polydon* for specimens from Maldiva and Laccadive Archipelagoes which chiefly differed from the former in possessing a corona ciliata. Fowler has combined these two and revised the diagnostic characters of the former.

This species markedly differs from all other sagittae by its larger numbers of anterior and posterior teeth. But many of them superficially resemble this species very closely and some of them like *S. neglecta*, *S. robusta*, *S. ferox*, *S. tenuis*, and *S. pulchra* are found along the East and West Coasts of South India. But this species can be clearly separated from them by some other easily observable characters. *S. neglecta* and *S. tenuis* distinctly differ from it by their longer distance between the genital openings. In *S. robusta* the corona ciliata does not extend so far toward the ventral ganglion. In *S. pulchra* and *S. ferox* the corona ciliata is equally long but in the former the anterior and posterior fins are very close together or touch each other and in the latter the anterior fin narrows slightly forward.

SAGITTA BOMBAYENSIS NOV. SP.

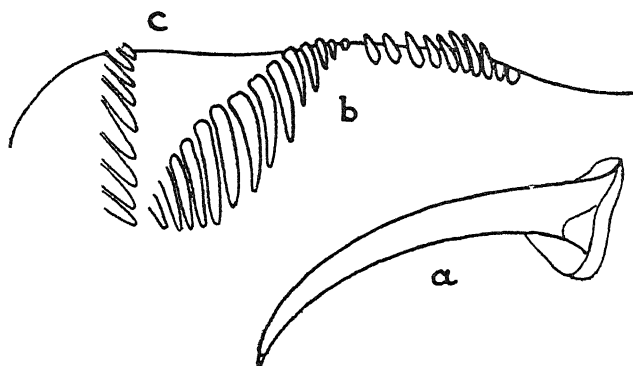
CHARACTERS: The body (Plate I, Fig. 3) is slender and often like a pin in shape. The head is broad and short but its breadth does not stand out as there is a thick collarette. The body wall is muscular and the body opaque in preservation. The collarette continues behind as a thin epidermal lining on the trunk. A little in front of the ventral ganglion the epidermis gradually thickens again and spreads out laterally to the beginning of the anterior fin. This thickening decreases gradually backward till it disappears in the middle of the tail segment. The trunk is columnar in its middle three-fifths and rapidly tapers forward and slightly backward. The constriction between the tail and the trunk is clearly seen. The tail is one-fourth of the body in length. The specimens vary from 4 mm. to 13 mm. in length.

The anterior fin is short and narrow and covered with the thickened epidermis along the base. It comes out of the latter at the beginning of the middle third of the body. It gradually widens backward and is a little less than one-fourth of the total length. The posterior fin is equally short and equally in front and behind the tail septum. Its widest part is in the middle of its caudal half and it gradually narrows forward. The anterior and posterior fins are separated by one-third of their length. The caudal fin is triangular with rounded corners.

There are 9 or 10 medium-sized curved prehensile spines (Text Fig. 3). The anterior teeth in large specimens vary between 8 and 12 and are arranged in a longitudinal row. The posterior teeth in large specimens vary between 16 and 25 and their row bends round backward to the mouth.

The corona ciliata is long, slightly sinuous and a little broad

anteriorly. It begins a little in front of the eyes and extends backward for two-thirds of the body in front of the ventral ganglion. The ventral ganglion is small and narrow and situated in front of the anterior fin at a distance of its own length. The tactile bodies are very numerous and arranged in many transverse rows. The sensory hairs give it a "hispid" appearance. They are also found on the caudal fin where they are arranged in two or four columns.



Text fig. 3—Armature of *S. bombayensis*, 13 mm. long, seen from the ventral side.

a, prehensile spine; b, posterior teeth; c, anterior teeth.

The intestine is straight and narrow. The ovaries are long and linear and may extend beyond the posterior end of the ventral ganglion. The oviduct opens to the outside on a small papilla. In the testes of mature specimens sperms and not their morulae are seen. The seminal vesicles in living specimens appear as white, opaque and glistening bodies attached to the tail. They are spout-shaped with their external openings being anterior and directed outward. In mature specimens they extend from the caudal to the posterior fin. The distance between the genital openings is about 12 per cent. in large specimens.

FORMULA OF *S. BOMBAYENSIS*

| Total length in mm. | Percentage of distance between genital openings in total length | Prehensile spines. | Anterior teeth. | Posterior teeth. |
|------------------------|--|-----------------------|--------------------|---------------------|
| 13 | 12 | 8 | 10 | 26 |
| 8 | immature | 8 | 5 | 11 |
| 5 | immature | 8 | 4 | 8 |

REMARKS: This species is present in the Bombay Harbour throughout the year but it appears in swarms during the South-West Monsoon.

It is characterised by the thickened epidermis nearly all through the length of the body. This thickened epidermis is seen even in very small specimens and distinguishes this species from all other species of *Sagitta* except *S. regularis* which is also provided with a similar thickening. The latter was described by T. Aida in 1897 from Japan and later recorded by Doncaster (1) from the Maldive and Laccadive Archipelagoes. According to Doncaster, "This species is very small, rarely more than 5mm....The tail is one-third of the length of the whole. ...It (corona) lies entirely on the trunk." This kind of corona has been drawn under the camera lucida by Fowler from a specimen of this species. The Bombay specimens markedly differ from this species on all these points and also in the absence of the epidermal thickening anteriorly on the head. These differences are sufficient to raise the local specimens to the rank of another species. But as remarked by Fowler, if *S. regularis* is not sufficiently observed and adequately described the local species may merge into it. We have therefore provisionally named it as *S. bombayensis* in order to point out its differences from *S. regularis* of Aida and Doncaster. Dr. C. C. John has kindly seen our specimens and approved of our plan.

The following table gives the numbers of the specimens of these species found in the largest catches of half-hourly tow-nettings of each month in the year 1933 and roughly indicates the seasonal variation in the population of these species in the Bombay Harbour at the surface.

| | Jan. | Feb. | Mar. | Apr. | May. | Jun. | Jul. | Aug. | Spt. | Oct. | Nov. | Dec. |
|-------------------------|------|------|------|------|------|------|------|------|------|------|------|------|
| <i>S. gardineri</i> ... | 130 | 20 | ... | ... | ... | 16 | 97 | 187 | 267 | 60 | 728 | 1028 |
| <i>S. bedoti</i> ... | 590 | 260 | 7 | 803 | 375 | 105 | 428 | 753 | 604 | 32 | 110 | 203 |
| <i>S. bombayensis</i> | 567 | 79 | 8 | 688 | 183 | 1336 | 1243 | 184 | 378 | 30 | 62 | 165 |

ACKNOWLEDGMENTS

We take this opportunity to express our indebtedness to the University of Bombay for financially helping us in this investigation. We have also to thank the Director of the Zoological Survey

PLATE I

Outline drawings by camera lucida

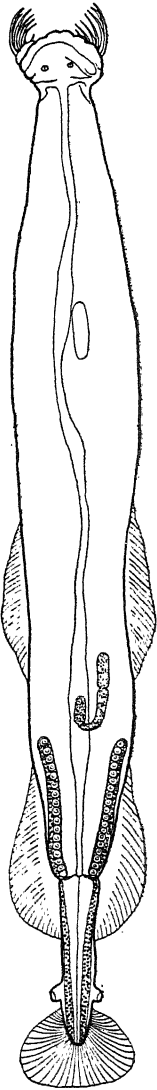


Fig. 1—*S. gardineri*
21 mm. long.

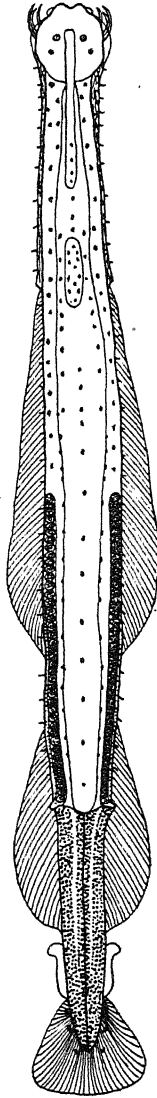


Fig. 2—*S. bedoti* 15 mm.
long.

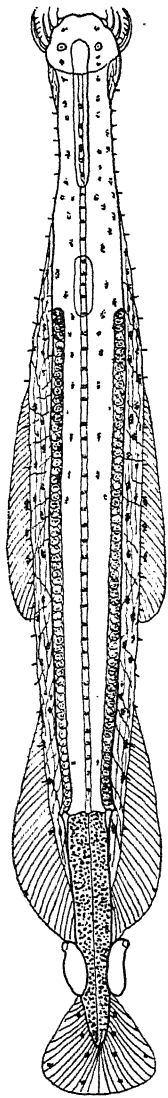


Fig. 3—*S. bombayensis*
13 mm. long.

of India and the Honorary Secretary of the Bombay Natural History Society for the loan of reference books.

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THE ANATOMY OF DENDROSTOMA SEIGNIFER
SELENKA ET DE MAN

(Continued from *Bom. Uni. Jour. Vol. III 5 pp. 102-113*)
(With 12 Text-figures)

BY

P. R. AWATI & L. B. PRADHAN
(Royal Institute of Science, Bombay)

THE BLOOD VASCULAR SYSTEM

The blood vascular system will be described under three separate heads, namely, the circulating fluid the blood, the vascular structures and the course of circulation.

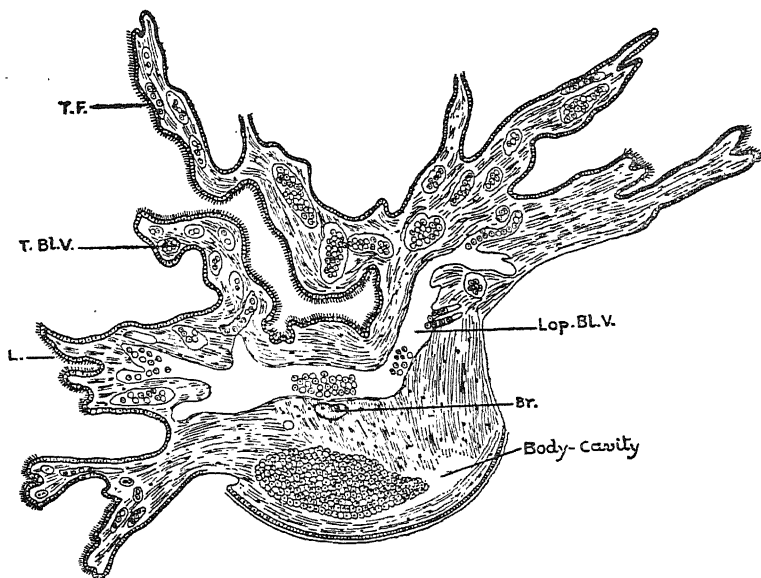
THE CIRCULATING FLUID. The blood which flows through the vessels is a madder red coaguable liquid containing numerous corpuscles in suspension. The plasma itself is colourless but the madder red colour of the blood is due to a kind of respiratory pigment—"haemerythrin" contained in the corpuscles which are of one kind only and similar to those smaller corpuscles found in the coelomic fluid of the body cavity.

THE VASCULAR STRUCTURES. The vascular structures principally include (1) the single dorsal vessel which is often called the heart (2) the circular or lophophoral sinus surrounding the pharynx anterior to the oesophageal nerve commissure (Fig. 1. Lop. Bl. V.) and (3) the tentacular blood vessels (Fig. 1, T. Bl. V.)

1. THE DORSAL BLOOD VESSEL. The vessel commences as a posterior median prolongation of the lophophoral sinus. It runs posteriorly along the mid-dorsal region of the pharynx and the oesophagus, and ends blindly at the place where the oesophagus takes an upward course. It can be divided into two parts according to the presence or absence of blind processes. In the first part of this vessel which is enclosed with pharynx and the oesophagus in the tube formed of the retractor muscles, there are no blind caeca, while in the second part it separates out from the sheath and gives out numerous blind caeca from all its sides.

The following are the histological elements in the dorsal blood-vessel (Fig. 1 A). The peritoneum (A.P.) forms the external layer while the innermost layer is formed by a distinct epithelial lining similar to that found in the tentacular vessels. Between these two layers there is a thin connective tissue, containing fibres—muscular as well as white connective tissue (A.P.) The connective tissue

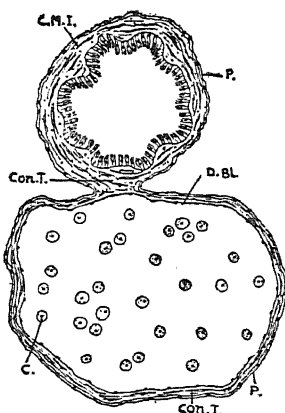
with the external peritoneal layer appears to be continuous with that on the wall of the oesophagus. This connective tissue between the oesophagus and the blood vessel may initiate the rhythmic contractions in the latter when the former is undergoing peristaltic movements.



Text fig. 1—An oblique section passing through the tentacular region $\times 40$.

Br: Brain; L: cilia; Lop. Bl. V.: Lophophoral blood sinus;

T. Bl. V.: Tentacular blood vessel; T. F.: Tentacular filament.



Text fig. 1A—T. S. Passing through the oesophagus and the dorsal blood vessel showing that the connective tissue of the oesophagus is continuous with that of the blood vessel.

C.: Blood corpuscle;

Con. T.: connective tissue;

D. BL.: Dorsal blood vessel;

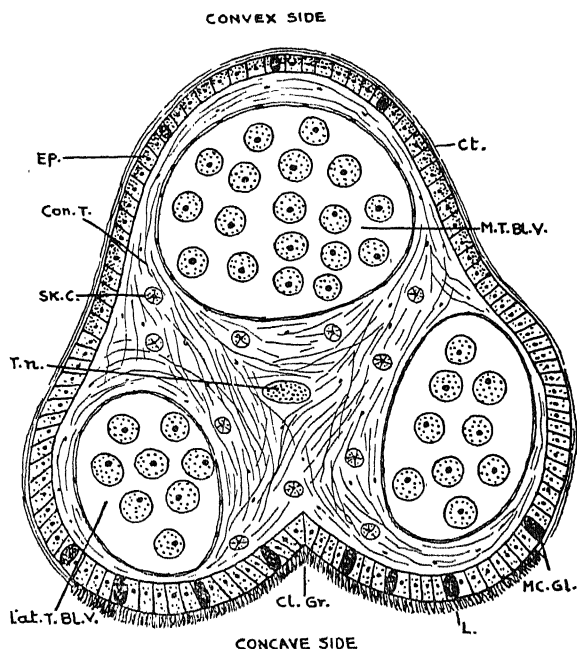
P.: Peritoneum $\times 400$.

2. THE CIRCULAR OR LOPHOPHORAL SINUS. This sinus surrounds the pharynx anterior to the oesophageal nerve commissure (Fig. 1 Lop. Bl. V.).

3. THE TENTACULAR BLOOD VESSELS. The filament appears triangular in shape with round corners in a transverse section.

Histology of the tentacular filament (Fig. 2). Externally each tentacle is covered over with a thin layer of the cuticle. Below it lies the epidermal layer, the epithelial cells of which are of two sorts :—

- (i) Ciliated columnar cells on the concave surface,
- (ii) Cubical non-ciliated cells on the convex and the lateral sides. These cells are covered over as already mentioned by the cuticular layer.



Text fig. 2—T.S. of a branchial filament showing the three tentacular blood vessels.

Cl. Gr. : ciliated groove; Con. T. : connective tissue; Ct. : cuticle;

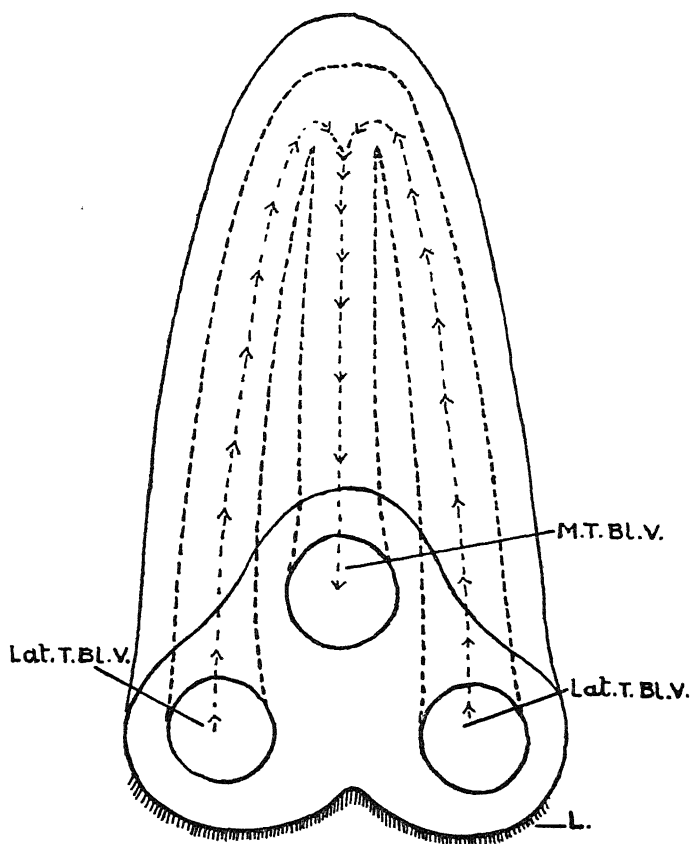
Dp. : Epidermis; L : cilia; Lat. T. Bl. : Lateral tentacular blood vessel; M. T. Bl. V. : Median tentacular blood vessel;

Mc. Gl. Mucous gland; S.K.C. : Skeletal cell;

T.n. : Tentacular nerve. $\times 400$.

There are a few unicellular glands on the convex side and in between the ciliated cells (Mc. Gl.). These glands seem to secrete mucus which forms a string which is washed into the mouth by the current of water and which entangles minute particles of organic substances of food and which therefore helps the animal in catching its food.

Below the epidermal layer is found the connective tissue which nearly fills the core of the tentacle. Enclosed in the connective tissue (Con. T.) are found three blood vessels one at each rounded corner. The middle of the blood vessel which is situated at the convex side is larger than the other two (M.T.Bl. V. ; Lat. T. Bl. V.) Each blood vessel is lined by a delicate layer of



Text fig. 3—A diagram showing the connection of the two lateral vessels with the median vessel at the apex in the tentacular filament : L ; cilia ;
 Lat. T. Bl. V. : Lateral tentacular blood vessel ;
 M.T.Bl.V. : Median tentacular blood vessel.

endothelial cells of which the nuclei are more prominent. The connective tissue consists of fine fibres traversing in all directions with a few prominent rounded cells with a distinct nucleus. These cells are similar to those described by Shipley¹ in *Phymosoma* as "Skeletal cells". Besides these there are also muscle fibres

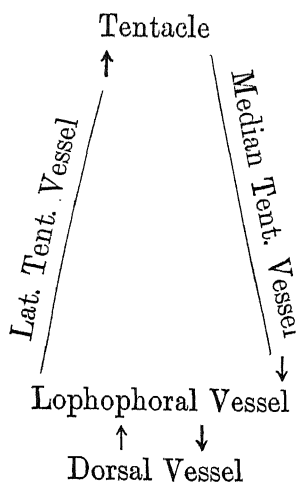
1. Shipley A. E. (1890) on *Phymosoma varians* Quarterly J. Micr. Soc. London. Vol. 31, p. 1.

embedded in the connective tissue. The tentacle is richly supplied with nerves. The main tentacular nerve given off from the circumoesophageal commissure runs through the connective tissue matrix of the tentacle. This nerve gives off numerous delicate branches to all the parts of the tentacular filament.

THE COURSE OF CIRCULATION: The dorsal blood vessel with its rhythmical contractions initiated by the peristaltic movements of the oesophagus is considered to act as the heart. A wave of contraction appears to start either at its anterior or posterior end and to drive the fluid slowly to the opposite end. The current after a very short time is reversed in its direction and then the blood is seen to be flowing in the opposite direction.

When the course of circulation is forward, the dorsal vessel empties its contents into the lophophoral sinus from which it goes to the tentacular vessels. The blood in the lophophoral sinus passes to each of the tentacular filament through the two lateral vessels and then turns back to the base of the filament through the single median vessel (fig. 3). After an interval of about ten to fifteen seconds the direction of the flow of the blood is reversed and some of the blood in the lateral vessels flows back to the lophophoral sinus, but the direction of the blood current in the median vessel remains all the while the same and is never reversed. Consequently the aerated blood is collected in the lophophoral sinus and when the direction of the peristaltic movements of the dorsal vessel is changed the lophophoral sinus empties its contents into it. Again after a lapse of about ten to fifteen seconds, there is a wave of contraction from behind and the whole process is repeated as before.

Diagrammatic representation of the course of circulation :



THE NERVOUS SYSTEM

The nervous system is divided into two main parts; the central and the peripheral. The former comprises the brain and the ventral nerve cord, while the latter consists of the nerves from the brain (the cerebral nerves), the nerves to the bodywall, and the nerve plexuses on the digestive tract, the spindle muscle, the bodywall, the retractor muscles etc.

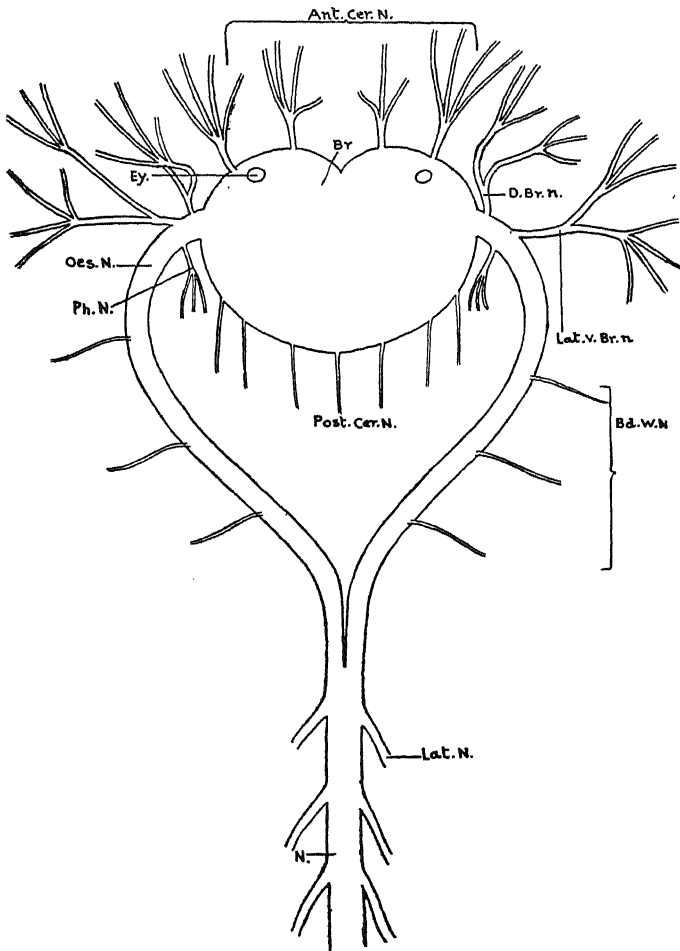
1. THE CENTRAL NERVOUS SYSTEMS:—The brain or the cerebral ganglia measuring about 0.6 mm. in a specimen of 3.7 cms. length has a heart-shaped outline although it is bilobed (Fig. 4 Br.). When viewed dorsally the posterior side appears to be convex while anteriorly are found two prominent lobes with a shallow groove between them. Close to its anterior margin are found embedded two small black spots usually spoken of as the "eyes" or the Sense pits (Figs. 4 and 6 Ey.). Their ventral surface is directly in contact with the dorsal vessel, while the ventro-lateral margins are abutting against the sides of the pharynx. The dorsal surface on the other hand is free in the body cavity.

The histological structure. The brain substance is made up of nerve fibres in the centre and nucleial cells at the periphery (Fig. 6). There are, however, no nerve cells towards the ventral margin, but it is mainly occupied by nerve fibres from the central region. This ventral margin as already stated above comes in contact with the dorsal blood-vessel.

The nerve cells are generally small with deeply stained central nuclei. They may be unipolar or bipolar. At the postero-dorsal angle of the brain are found a few peculiar bodies known as "giant cells". These cells are about four times bigger than the ordinary nerve cells and are generally unipolar. They are more or less pear-shaped and their nuclei are relatively smaller in proportion to their bulk and are located towards the base. Such giant cells are not, however, found anywhere else in the nervous system.

The Ventral Nerve cord: The ventral nerve cord is formed by the meeting of the two circumoesophageal commissures issuing one from each side of the brain (Fig. 4. Oes. N.). After its formation, it shows no trace at all either of its division into two halves as in annelids or concentration of nerve cells in any particular region or places along its course. It is attached throughout the ventral bodywall partly by the peripheral nerves and partly by the connective tissue sheath which forms the external covering as it runs along the ventral surface of the body as a straight filament. It is somewhat flattened in the region of the introvert while it gradually becomes cylindrical towards the posterior end where it

terminates in two or three unsymmetrical slender nerves which enter the bodywall. There is no ganglionic swelling at the termination of the cord as in *Sipunculus*'.



Text fig. 4—The Central Nerve System.

Ant. Cer. N. : Anterior cerebral nerves; Bd. W. N. : Nerves to the bodywall; Br : Brain; D. Br. N.: Dorsal branchial nerves; Ey : Eye; Lat. N.: Lateral nerves; Lat. V. Br. n. : Lateral and ventral branchial nerves; N. : Ventral nerves; Oes. N. : Circumoesophageal nerve; Ph. N. : Pharyngeal nerve; Post. Cer. N. : Posterior cerebral nerves.

The Structure of the Nerve cord : In a transverse section the structure of the nerve cord appears to be as follows: Externally there is a peritoneal membrane; next to it on the inside is formed a thick connective tissue in which are seen fibres and nuclei of the two bundles of the longitudinal muscle fibres in the

lateral aspect of the cord. Then comes the central nervous mass, in which nerve cells are aggregated on the ventral side of the cord and the fibrous mass on the dorsal. This arrangement is quite the reverse of that found in the brain substance.

The lateral longitudinal muscle fibres in the connective tissue of the nerve cord bring about the contraction and extension of the cord corresponding with the movements of the bodywall of the animal.

II. THE PERIPHERAL NERVOUS SYSTEM. It consists of (1) cerebral nerves and (2) nerve rings from the ventral nerve cord in the bodywall and (3) the nerve plexuses.

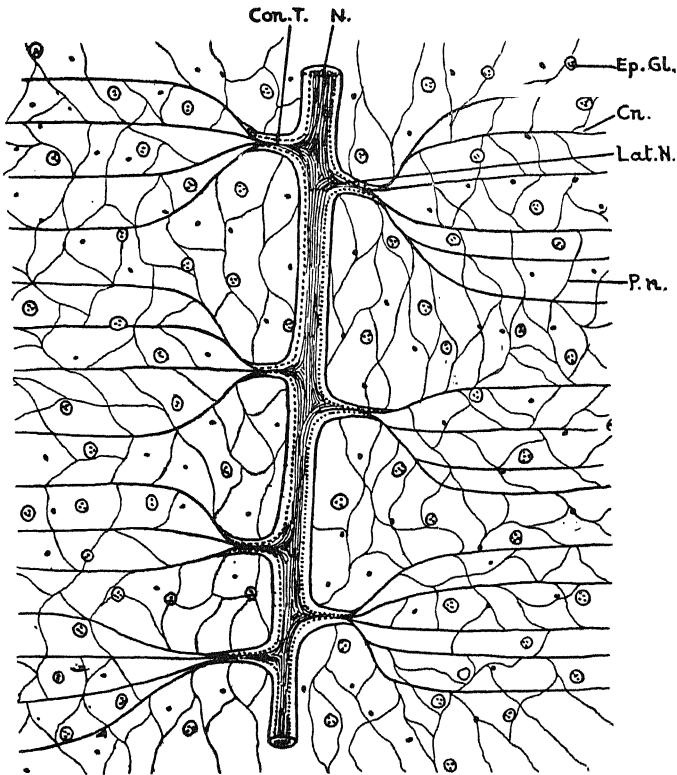
(1) *Cerebral Nerves* :—(a) anterior cerebral nerves : From the anterior convex lobes of the brain are given small nerves two on each side of the groove which supply the skin of the anterior region of the animal (Fig. 4 Ant. Cer. N.). (b) Posterior cerebral nerves : From the posterior part of the brain are given off numerous nerves to the retractor muscles. The large circumoesophageal commissure also gives out after encircling the pharynx meets its fellow from the other side to form the ventral cord. Each of them supply nerves to the anterior parts of the body.

Three nerves are given from each of the circumoesophageal commissure. The first supplies nerve to the dorsal branchiae (D. Br. n.) The second nerve which is perhaps the largest arises from the middle of the commissural nerve and supplies the lateral and the ventral branchiae (Lat. V. Br. n). These tentacular nerves branch out on their course and one branch is supplied to each filament of the tentacle, the nerve filament running through its centre of the filament beneath the ciliated groove (Fig. 2. T. n). The third commissural branch which is shorter arises from the postero-ventral side and supplies nerves to the pharynx (Fig. 4 Ph. N.). Numerous small nerves are given off to the body-wall from the lateral side of each of the circumoesophageal commissural nerve before it forms the ventral nerve cord (Fig. 4. Bd. W.N.).

Nerve rings from the ventral nerve cord in the body-wall. There are innumerable lateral nerves arising along the whole length of the cord on both sides but there is no indication of any metamerism or regular repetition of any kind in the arrangement of their nerves (Fig. 5). Each nerve takes its origin from the lateral side of the nerve cord. It is surrounded at its base (before it divides), by a thin connective tissue sheath, containing a few elastic fibres (Con. T). Each lateral nerve first passes outward and immediately bends ventrally to enter the body-wall. It then divides and carries branches in between the two layers of the bodymuscles. Each

branch of the lateral nerve runs from one side of the cord to the other along the dorsal aspect of the body, thus almost encircling the latter (Cn). The ring is, however, not complete as it is on the ventral side below the nerve cord.

The bodywall is richly supplied with a network of these nerve rings. Each of them is subdivided and each subdivision supplies



Text fig. 5—Surface view of the skin showing the network formed by lateral nerves.

C. n. : Circular nerve fibres ; Con. T. : Connective tissue ; Ep. Gl. : Epidermal gland ; Lat. N. : Lateral nerve ; P. n. : Peritoneal nerve plexus $\times 40$.

a particular area, such as the peritoneal layer, (P. n.), the sub-epidermal area etc. In the sub-epidermal area, however, the nerves form an intricate network which supplies nerves to the epidermal organs.

3. NERVE PLEXUS : They are found at different places forming the sub-epidermal plexus, the plexus on the wall of the alimentary canal, plexus on the retractor muscles etc.

SENSE ORGANS

The Epidermal organs or "The Sense papillae"—The whole of the external epidermal layer is sensory, that is, tactile in function but there are a few localised sense organs of which the structure and position is already described in connection with the epidermis and its organs in the first part. The function of these organs seems to be both sensory and protective. Their cells secrete mucus for covering and ultimately removing foreign bodies attached to the external surface of the animal and play an important rôle in bringing about the contraction of the whole body, thus exposing the minimum surface of the animal to the outside world. The contraction of the animal which is effected by a nervous mechanism is described below.

Each cell is provided with a sensory hairlike process at the distal end. This process is connected with the sub-epidermal nerve plexus which is linked with the nerve rings. The latter as described above from the main branches given off from the ventral nerve cord. At the slightest disturbance at the external surface of the body, the sensory stimulus which is carried to the ventral nerve cord, through several connecting nerve links causes the contraction of the longitudinal body muscles and thereby brings about the shortening of the whole body.

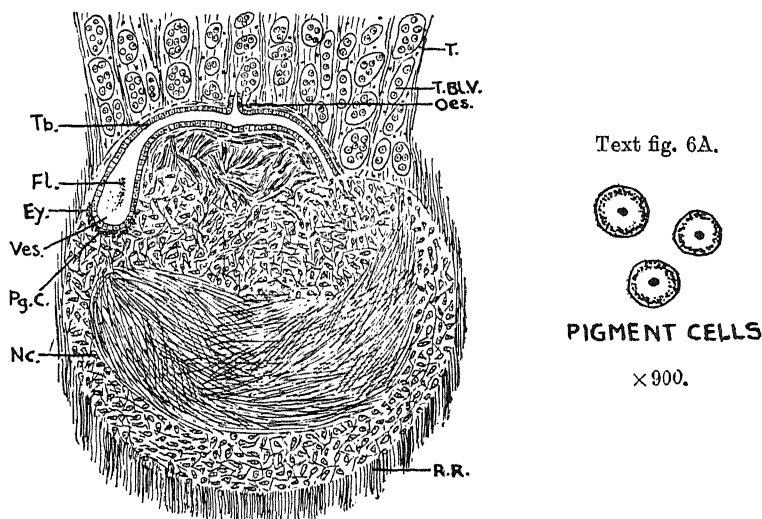
There is a difference, however, in the nature of the stimulus and hence the response is also different. A slight disturbance or irritation at any external surface of the body may cause only secretion of mucus from the cells of the papillae to flow at that region, in order to remove the source of irritation, but the continued disturbance at the same place may bring about the contraction of the whole body through the nervous mechanism already described.

Another function which has been attributed by some observers to these glandular cells is that their secretion seems to soften and to dissolve soft parts of stones or coral rock in which sipunculoids burrow¹.

2. The "Sensory pits" or the "Eyes". These sensory pits which are sometimes referred to as "eyes" are not well developed in this animal. They constitute a pair, one at each antero-lateral margin of each lobe of the brain (Fig. 4 Ey.)

1. Shipley A. E. (1890). *Phyrosoma varians* quarterly J. Mier. Soc Vol. 31. p. 1.

Each sensory pit (Fig. 6) consists of two parts. Pigmented vesicular swelling (Ves) embedded in the substance of the brain and tubular structure (6 Tb.) in continuation of the swelling. The tubular portion passes outwards and horizontal to the long axis of the body, upto the mid-dorsal line, to meet the one from the other side and then to open by a common short vertical channel into the oesophagus (oes) just anterior to the cerebral lobes. The vesicular swelling embedded in the substance of the brain contains a homogeneous co-agulable fluid (Fl.), probably a product of secretion of its living cells.



Text fig. 6—Horizontal section of the brain showing the origin of the duct from each of the sensory pits and their common opening into the oesophagus $\times 40$.

Ey : Eye ; Fl : Fluid ; Nc. : Nerve cell ; Oes : Oesophagus ; Pg. c. : Pigment cell ; R. R. : Retractor muscle ; T : Tentacle ; Tb : Tubular Portion ;

T. Bl. V. : Tentacular blood vessel ; Ves : Vesicular portion.

HISTOLOGICAL STRUCTURE. The layer lining the sensory pit is one cell thick. The cells are elongated, more or less columnar with granular protoplasm and the nucleus at the proximal or narrow end of the cell. None of these cells is ciliated as described in the "cerebral organs" of other sipuneuloids. The arrangement of these cells seems to be more definite towards the inner or the vesicular portion.

The vesicular swelling of the sense pit organ is linked with a layer of pigment cells (Fig. 6 and 6A Pg. e.) four to five cells thick. Each cell is round having a prominent nucleus at the centre. The pigment granules are, however, restricted towards the outer

periphery of the cell. The black colour of the sense pit which is seen from outside is due to these pigment cells.

Functions of the Sense Pits. From its relation with the oesophagus, the nature of the function of these sense pits seems to be different from that of similar "cerebral organ" either of sipuneulus or phymosoma. In the case of Phymosoma it is said that these act as rudimentary eyes to distinguish darkness from light¹. Therefore pigment cells in Dendrostoma are not photosensitive and therefore cannot be regarded as photoreceptors. Obviously they cannot function as visual organs as vision requires, the projection of a focused image of the source of light upon suitable photoreceptors. At the same time the presence of pigment cells cannot be explained satisfactorily. It may be that the black pigment may not always respond to light stimulus.

Another function attributed sometimes to these organs, in other Sipuneuloids, is that, they are tactile and sensory in function. But since the sense pits in Dendrostoma are in no way connected with the outside world and they open into the oesophagus, it is futile to suggest that they also perform the similar function here.

They may act as statocysts or balancing organs as in other animals such as mollusca.

It may be strongly presumed that they may act as water testing organs. The water that passes through the oesophagus into the alimentary canal may be tested at the spot where these organs open into the oesophagus and in the case of unsuitable water, the mouth may be closed and this water may no longer pass into the alimentary canal. This sense organ can favourably be compared to the Jacobson's organ in the craniata or the osphradium in mollusca.

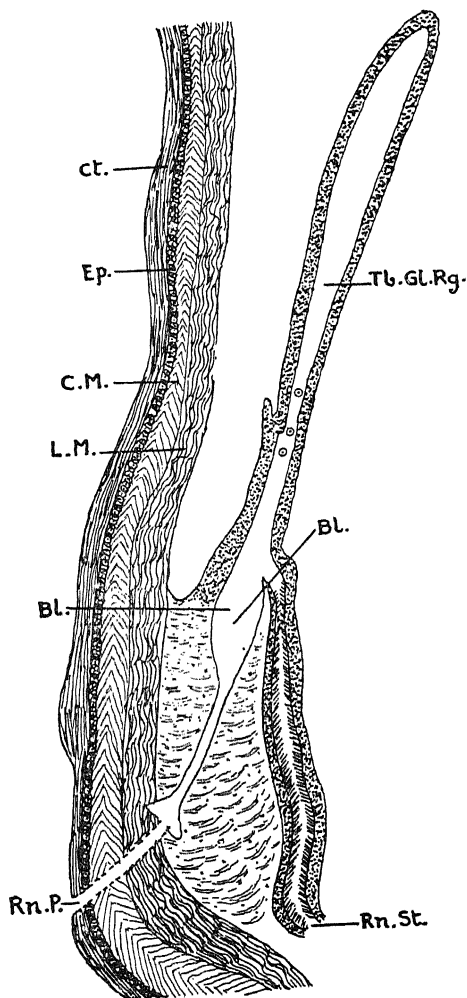
THE EXCRETORY SYSTEM

In Dendrostoma the nephridia or the excretory organs are in the form of a single pair of "brown tubes". They are situated far forward at the anterior end of the animal, their external openings (nephridiopores) being a little posterior to that of the anus. They lie on either side of the mid-ventral line, a little distance away from the nerve cord.

Each nephridium is nearly a straight tube of a yellowish colour, very mobile in the living condition and due to the muscle coat of its wall, the organ is capable of being shortened and elongated and also of twisted into a variety of shapes. The body of the nephridium hangs free in the coelom from the point of its attachment to the body-wall at the external opening.

1. Shipley, Cambridge Natural History Vol. II, 1901, p. 417.

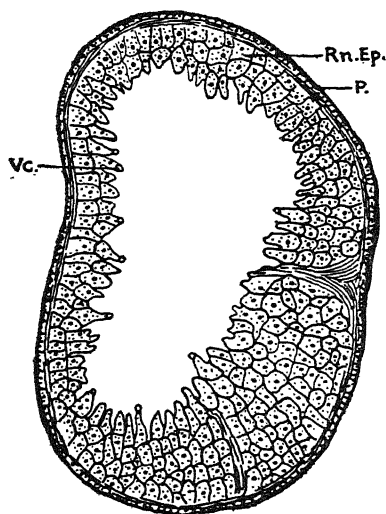
In each nephridium (Fig. 7) three separate regions can be recognised. The nephrostome region commencing with a funnel like orifice fringed with long cilia and opening into the body cavity, the body of the nephridium which is tubular and glandular region (Tb. Gl. Rg.), and the nephridiopore region which is a muscular sac opening to the exterior by the nephridiopore through which the products of excretion are from time to time thrown out by the contraction of its walls.



Text fig. 7—L. S. of brown tube showing the arrangement of the internal and external openings.

Bl. : Bladder ; C.M. : Circular muscle layer ; Ct. : Cuticle ; Ep. : Epidermis ;
L. M. : Longitudinal muscles ; Rn.P. : Nephridiopore ; Rn.St. : Nephrostome ;
Tb. Gl. Rg. : Tubular glandular region $\times 40$.

The Nephrostome and the nephridiopore. The nephrostome (Rn. St.) consists of a ciliated lip and is situated near the external opening (Rn. P.). The external opening is situated just behind the internal and communicates with the outside by a short neck leading from the bladder (Bl.) to be described later. The nephridiopore (Rn. P.) situated at the ventro-lateral aspect of the body is surrounded by a thickened ring of connective tissue intermixed with circular muscle fibres forming a sphinkter. The close proximity of these two pores the nephridiopore and the nephrostoma seems to indicate that the nephridium is doubled upon itself during the course of development. The body of the nephridium may again be divided into two parts, namely, the anterior swollen and nonglandular region the bladder (Bl.), and posterior glandular portion of the body the posterior prolongation of the bladder. The diameter of the bladder is about three or four times that of the posterior tubular portion, the single lumen of which is, however, partially divided by a number of septa projecting into it.



Text fig. 8—T.S. of the brown tube passing through the glandular region.

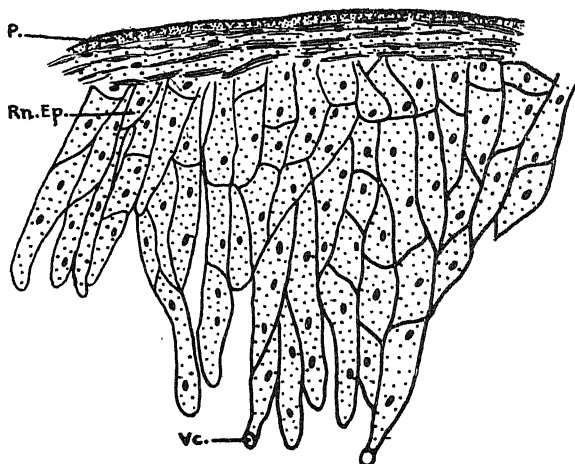
P : Peritoneum ; Rn. Ep : Renal epithelium ; Ve : vesicle. $\times 200$.

Minute histological structure of the body of the Nephridium.

(a) The bladder. Three layers can be recognised in the wall of the bladder, namely, the external peritoneal layer, the middle of irregularly arranged muscle fibres and the innermost single layer of cubical cells.

(b) Tubular glandular portion. (Figs. 8 and 9). Externally the nephridium is covered by the peritoneum some of the cells of which are ciliated (P.). This layer is essentially distinguishable from the nephridial cells by its avidity for staining reagents and also by the absence of secreting granules.

Next to the peritoneum there is a thin layer of connective tissue matrix in which are found strong circular and longitudinal muscle fibres. The internal epithelium consists of cells in many tiers which project into lumen of the tube (Rn. Ep.). The cells are extremely long and are loaded with fine yellowish granules which seem to be waste nitrogenous products of the body-fluid. In living animals these cells are found to possess at their distal extremities many large thin walled vesicles (Ve.), which are thrown off from time to time into the lumen of the tube. These vesicles in the lumen resemble more or less drops of oil, when examined in a living condition. It is probable that the excretory products of the nephridial cells are stored up in these vesicles before being discharged together with the vesicles themselves.



Text fig. 9—A portion of the same seen under a high power.

P : Peritoneum ; Rn. Ep. : Renal epithelium ; Ve : Vesicle. $\times 270$.

The hemispherical cups or depressions between the flattened epithelium, described by Shipley in *Phymosoma*, are absent in this animal¹. The excretory soluble products appear to be absorbed directly through the peritoneal layer into the nephridial cells and form vesicles while the nephrostome of the nephridium functions as the inner opening of a gonoduct.

1. Shipley A. E. (1890). On *Phymosoma* varians. J. M. S. Vol. 31, p. 1.

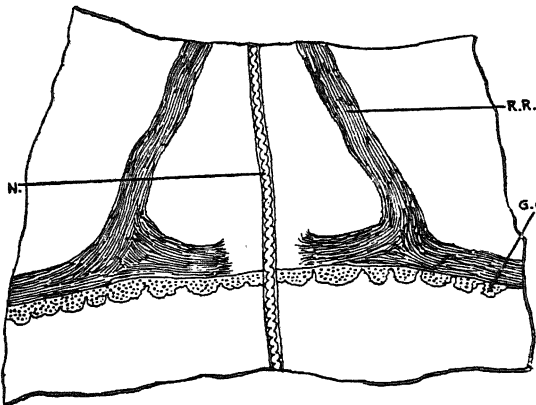
Other solid elements besides the vesicles in the lumen of the body of the nephridium are eggs in the female and spermatozoa in the male, and also the coelomic corpuscles. The presence of the latter escaped the notice of many observers who have therefore maintained that the nephrostome has the power of selecting the generative cells only when they come within their reach while they reject coelomic corpuscles.

As a rule two is the normal number of nephridia, but some five or six stray cases are met with in which the animals are found to possess sometimes three nephridia two on one and one on the other or at times only, that on the right or left being absent.

Besides being excretory, the nephridium acts as a gonoduct, the genital cells, either ova or sperms are taken in through the nephrostome and discharged to the outside through the nephridiopore.

REPRODUCTIVE SYSTEM

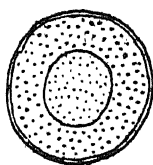
The animal is uni-sexual. There are no external characters by means of which the two sexes can be distinguished from outside. In both males and females, there is absolutely no difference either in size, shape or colour of the animal. The testis and ovary are found in the same position in the two sexes and cannot be distinguished from each other without the aid of a microscope. Each gonad forms a transverse ridge at the posterior edge of the retractor muscle, near its attachment to the body-wall and extends across the median line just below the ventral nerve cord (Fig. 10, G.O.) This ridge is formed of modified peritoneal cells which



Text fig. 10—A view of the generative organs at the base of the two retractor Muscles (R. R.). The ventral nerve cord (N.) lies between the muscles and the generative ridge.

became modified, in the case of female, into ova and in the case of male into the mother cells of spermatozoa. The free end of the genital ridge is irregular and this irregularity gives it a frilled appearance.

Eggs break away from the ovary in their early stage of development, but they increase in size whilst still floating in the nutritive coelomic fluid. Each of them is round in shape, with granular protoplasm and a prominent central nucleus which occupies the major portion of the egg (Fig. 11). The latter secretes a thick membrane around its body. There is no micropyle.



Text fig. 11

Like the eggs the mother cells of spermatozoa break away in an immature condition and attain development in the coelomic fluid. Each of them has a rounded head from 2 to 2.5μ in diameter and a short spinous process at its anterior end, (Fig. 12, Sp.) while at the other end there is a long tail of about 300μ to 400μ in length (Fig. 12. t).

When the reproductive cells are completely developed they make their way into the lumen of the brown tube. The exact way in which this is accomplished is not clear. But the old idea, that the internal opening has the power of selecting generative cells only, when they come within its reach while it rejects the coelomic corpuscles, is entirely erroneous. The coelomic corpuscles are clearly seen in the lumen of the nephridium though they are a few in number compared with reproductive cells. This paucity of the corpuscles may be due to their being disintegrated in the lumen of the nephridium.



Text fig. 12

With regard to the proportion of sexes in this animal, it is found that the number of females is predominantly large over the males. The proportion of males to females can roughly be stated as 1 : 60. This is not a phenomenon peculiar to this animal only. As will be seen from the following observations of previous workers, that the relative abundance of one sex over the other is also common in other Sipunculoids. For example Keferstein in 1862 noticed much disparity in the relative number of males and females of *Phascolosoma*. Only two individuals with spermatozoa were found among 200 specimens of females with eggs.

Claparede in the following year, found only one male in 112 females, and this one of a different species.

This disparity may be due to one of the following facts :

- (1) Animal may be male first and then become female throughout its life (Protandry).
- (2) Males may be extremely minute escaping observation.
- (3) There may be facultative parthenogenesis.

Owing to the extreme rarity of the male, it was found difficult to make any investigation with regard to the embryonic development of the animal.

Experiments on artificial fertilization are being made. The results are not as yet definite to be announced here.

List of theses which have been accepted in lieu of the Examination for the Degree of M.Sc. in Biological Sciences during the Year 1935-36

| Subject | Title of thesis | Name of the candidate | Teacher | Place of research | Remarks. |
|-------------|---|-----------------------|----------------------------|------------------------------------|--|
| Botany ... | A study of the Gametophyte of <i>Ophioglossum</i> from Poona. | Mr. T. S. Mahabale | Prof. D. L. Dixit | Ferguson College, Poona | |
| | The Nature and Bio-chemical action of the Fungus Flora of the Soil. | Mr. P. K. Anjaria | The Rev. G. Palacios S. J. | St. Xavier's College, Bombay | |
| | A contribution to the knowledge of the life history of <i>Naias Graminea</i> Del. | Mr. C. M. Patel | Prof. S. V. Shevade | Baroda College, Baroda | |
| | The study of the periodical changes in the Hydrogen Ion concentration of the cell sap and in the Isoelectric point of the proteins of the cotton plant. | Mr. S. V. Mensinkai | Prof. R. H. Dastur | Royal Institute of Science, Bombay | |
| | The Structure and Bionomics of <i>Harpodon nehereus</i> (Ham. Buch.) | Mr. F. Max Pinto | Prof. P. R. Awati | Royal Institute of Science, Bombay | In preparation for publication. |
| Zoology ... | The Anatomy and physiology of the water-bug <i>Sphaerodema rusticum</i> Fabr. | Mr. M. J. Presswalla | Prof. C. J. George | Wilson College, Bombay | Published partly in this issue & partly in Proc. Ind. Acad. Sci., 11, pp 280-315 |

Reviews

Midwifery by Ten Teachers, under the direction of Clifford White.

Ed. by Sir Comys Berkeley, J. S. Fairbairn and Clifford White. Fifth edition. (Arnold & Co.) London, 1935. 18s. net.

The book has been admirably written for the student and proves without doubt of much practical use to him even afterwards in his practice. It is the fifth edition and no pains have been spared to bring information up to date especially about the functions of the anterior pituitary lobe and the ovary and their bearings on menstruation and pregnancy, about Aschheim-Zondek test and its utility in diagnosing Vesicular mole, about Toxaemia of pregnancy and puerperal sepsis. It is adequately illustrated, but to attain completeness some more figures are wanted on lower segment operation, described with classical Caesarian section, as it is often resorted to nowadays, especially in test labours; and the student will find it easy to understand its technic by the help of such illustrations. Again, there seems to be a mistake in naming different planes on Fig. 45, page 224. The plane of the anatomical outlet has been called 'the plane of least pelvic dimensions' and vice versa, an oversight which may be revised in the next edition.

In the management of face presentation, a description is given for converting the face into vertex. At the outset it has been mentioned, "such methods may do harm by precipitating rupture of the membranes.....the face presentation is likely to recur....." Yet a method is described, although in the following para, while summing up the position, it is mentioned 'though success is unlikely'. The description of such a doubtful and impracticable method may better be dropped. It will be to the advantage of the student from examination point of view.

In the treatment of eclampsia for the control of fits, opium up to two grains in twenty-four hours has been advised but it can be conceded that limitations have also been laid down. However, what has been found here is that whenever the drug is given more than one grain, even when the initial dose of morphia may be gr. $\frac{1}{4}$, the respirations are lowered, seven or eight per minute and sometimes stopped and artificial respiration has to be resorted to and kept up for hours together. Even Dr. Fitz Gribbon has expressed

his views against such a big dose. Knowing the limit to be reached and forgetting the qualifications hedged round the administration of morphia, practitioners do in their dismay inject at short intervals morphia in order to bring fits under rapid control without waiting reasonably to see the effects produced by the initial doses. Again other drugs, such as Sodium Luminol by injection or Chloral Hydras per rectum, may be employed to supplement the effect of the effective dose of morphia, which avoids the dangerous influence of morphia on the respiratory centre and at the same time the fits can be controlled. So to err on the safe side and to prevent practitioners merely remembering the dangerous limit, which they recklessly rush to reach without using discretion, the dose advocated in such a standard text-book should not be more than a grain. Even Stroganoff does not advise more than $\frac{2}{3}$ gr. of morphia in 14 hours, given in combination with Chloral Hydras.

With all these minor points, as has been already mentioned, the book is the real text-book for the student, meeting his demands in all respects. It richly deserves the great popularity that it has rightly earned in the student world.

N. A. P.

Lectures on Diseases of Children by Robert Hutchison ; 7th Edition. (E. Arnold) London, 1936. 21s. net.

These lectures were delivered by the author to his students at the London Hospital. Even in cold print, they have still retained all the interest, information, lucidity and attractiveness that one invariably finds on hearing these learned discourses delivered by such an erudite scholar, acute observer and Clinician, and a refined lecturer. This Seventh Edition has been thoroughly overhauled and brought up to date. Perusal of this book would create sufficient interest in this important branch of medicine and the detailed discussion of treatment would be very valuable to the student and practitioner alike. The book has already established its well-merited popularity and good wine needs no bush.

B. G. V.

Text Book of Biology by E. R. Spratt and A. V. Spratt, published by Universal Tutorial Press, London, 9/6.

The authors have written this text-book of biology for the benefit of students completing their secondary education and preparing for Intermediate Science and Medical Entrance Examination of British Universities. Both the authors have taught the

subject for many years and treated it lucidly and exhaustively in this book.

They have arranged the treatment of plant and animal types so as to bring out how these two kinds are the outcome of the same life activity and how they live in associations for mutual advantage. A chapter is devoted to the chemical messengers of the animal body and the chapters on the physiology of plants and animals describe many simple illustrative experiments.

The value of the book would have, however, enhanced if the last chapter dealing with evolution, heredity etc. had been considerably increased.

S. H. L.

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